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THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS SOLUTION AS AFFECTED BY THE PRESENCE OF CERTAIN OTHER SALTS WITH LARGE HYDRATING POWER.

By Harry C. Jones and Horace S. Uhler.

(SEVENTEENTH COMMUNICATION.)

(*Continued from the February number.*)

The photographic strip adjacent to the numbered scale corresponds to the solution which did not contain any of the calcium salt. The second strip corresponds to the solution of concentration 0.271, and so on, until, finally, the strip next to the comparison spectrum pertains to the most concentrated solution in the series. The depth of the cell was 1.41 cm. for the Nernst film and spark. The spark line of shortest wave length recorded by the negative for the most dilute solution was 3436.9, but the continuous background barely extended to 0.347 μ. For the solution of concentration 4.041 transmission is shown by the negative, and began at 0.506 μ. Since the successive differences in concentration of the first 15 solutions are all equal, the spectrogram shows at a glance the dependence of the limit of absorption of the region which included the ultra-violet, upon the concentration of the dehydrating agent. That the locus of the left-hand ends of the photographic strips is, as would be expected, not a straight line, but a decided smooth curve, is very apparent. In fact, the band increased in width at the only measurable end by approximately 160 A. U., as the concentration changed from 0.271 to 0.541; but this limit of absorption only moved by about 65 A. U., as the concentration passed from 3.518 to 3.788. In other words, the less refrangible end of the ultra-violet band seems to tend towards a definite limit, as the concentration of the calcium chloride increased. That this absorption is primarily due to the copper chloride, and not to the ultra-violet band of the calcium salt, as such, follows at once from a consideration of plates III(*b*), V., and XI(*b*), and the remarks on the corresponding pages. The change in color of the solutions from blue to green, with increasing amount of calcium chloride, simply means that the ultra-violet band, which did not encroach upon the visible spectrum in the case of the blue solutions, had advanced into the visible spectrum and absorbed the violet and blue to a greater or less extent in the cases of the green and greenish yellow solutions.

Eye observations of the solutions were made with the aid of the cell having 2 compartments. The data thus obtained for the shorter wave length confirmed, then, in detail all the statements made above and derived from the photographs. Each one of the 16 solutions absorbed the red and orange completely. The more refrangible end of this band moved so gradually to shorter wave lengths, that it was only possible to see a very slight shift when the spectra of 2 consecutive members of the set of solutions were viewed simultaneously, but it was not possible to assign a number to the magnitude of the displacement. The best that could be done was to observe the extreme members of the series at the same time, and to obtain the average shift of the visible end of the band by dividing by 15.

The penumbra of the band in question appeared to have the same intensity at 0.640 μ, for the most dilute solution, as at 0.628μ for the most concentrated solution. Therefore, the mean observed displacement was 8 A. U. When the last-named solution was compared with distilled water, it was observed that the spectrum transmitted by the water had about the same intensity at 0.760 μ as the penumbra for the solution at 0.628 μ. Also, the solution did not transmit any color as completely as the water; *i. e.*, the former possessed appreciable general absorption between the regions of complete extinction of light.

The freezing point lowerings for the solution containing the chlorides of copper and of calcium are given in the following table:

1. Concentration of $CaCl_2$ in the mixture.	2. Concentration of $CaCl_2$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $CaCl_2$ alone were present.	5. Molecular lowering of freezing point if $CaCl_2$ alone were present.	6. Molecular lowering of freezing point for $CaCl_2$ in water alone.	7. Column 5 minus column 6.
0.398	0.000	20°.433	—	—	—	—
"	0.271	4°.305	1°.872	6°.91	4°.98	1°.93
"	0.541	6°.109	3°.676	6°.80	5°.32	1°.48
"	0.812	8°.28	5°.847	7°.20	5°.92	1°.28
"	1.082	10°.50	8°.067	7°.46	6°.54	0°.92
"	1.353	13°.10	10°.667	7°.88	7°.18	0°.70
"	1.624	16°.50	14°.07	8°.66	7°.88	0°.78
"	1.894	20°.75	18°.32	9°.67	8°.64	1°.03
"	2.165	26°.00	23°.57	10°.89	9°.75	1°.14
"	2.435	31°.25	28°.82	11°.84	10°.63	1°.21
"	2.706	37°.5	35°.07	12°.96	11°.70	1°.26
"	2.977	44°.0	41°.57	13°.96	13°.05	0°.91
"	3.247	52°.5	50°.07	15°.42	14°.32	1°.10
"	3.518		—	—	—	—

As the temperature of the green and yellow-green solutions decreased, the color became bluer. The solution of concentration 3.247 was very viscous and jelly-like near its freezing point. The freezing point lowerings of the last 3 solutions of the series could not be determined, since the salts separated out when the attempt was made to freeze the solutions.

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[1] Interpolated from the results of Jones and Bassett: THIS JOURNAL, 33, 546 (1905).

The electrical conductivities, together with the corresponding concentrations of some of the solutions containing copper chloride and calcium chloride are given in Table IX. The conductivity data are expressed in reciprocal ohms and reciprocal centimeters.

Table IX.

Concentration.	Conductivity.	Concentration.	Conductivity.
0.000	0.02938	1.624	0.08643
0.271	0.04601	1.894	0.08864
0.541	0.05586	2.165	0.08955
0.812	0.06512	3.518	0.07937
1.082	0.07320	3.788	0.07222
1.353	0.08146	4.041	0.06517

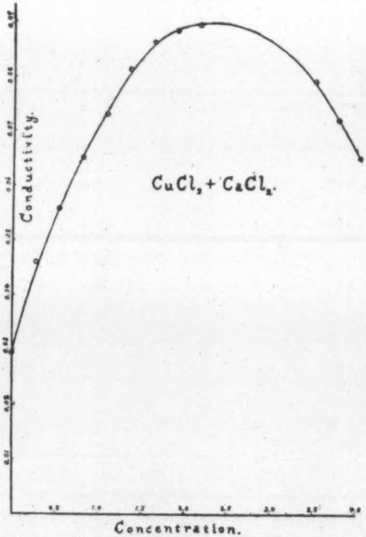


Fig. 12.

The data in the above table are plotted in Fig. 12. The abscissae and ordinates denote, respectively, concentration and conductivity. This curve has a well-defined maximum, just like all the preceding curves.

A peculiar difficulty presented itself when an attempt was made to determine the ohmic resistance of certain of the solutions containing copper chloride, and either calcium chloride or aluminium chloride. The resistance, aside from the cell constant, was first large and then decreased to a definite fixed value. For illustration, the successive resistances of the second solution recorded in the above table were 719.6, 716.9, 703.9, 704.3, 703.8. In all cases, the mean of 3 or more determinations, made after the solution seemed to have reached a steady state, was taken as representing the true ohmic resistance of the solution under investigation. This phenomenon could not be ascribed to changes in temperature, to air bubbles, to absorption of the electrode, or to variable resistance and contact in the electrical circuit. This was shown by repeated and careful tests of all of these matters, as well as of such other causes for the trouble as were thought of from time to time. It was not consistent with the investigation as a whole to pursue this question further.

Copper Chloride and Calcium Bromide.—(See Plates XIV(*a*), XIV(*b*), XV(*a*), XV(*b*), XVI(*a*) and XVI(*b*). Plate XV(*a*) and XV(*b*) is reduced to three-fourths of the original size.) The concentration of the copper chloride in all of the solutions was the constant 0.398. The concentrations of the calcium bromide were 0.000, 0.254, 0.508, 0.763, 1.017, 1.271, 1.525, 2.033, 2.542, 3.050, 3.389, 3.804. The first 6 increments of concentration each equal 0.2542, and the next 3 each equal 0.5084. The one next to the last has the value 0.339, and the last difference equals 0.415. The concentration of the solution of calcium bromide was 4.236. As the concentration of the dehydrating agent increased, the color of the solutions changed from pale blue to deep greenish brown, passing through all intermediate shades of bluish green, clear green and yellowish green. Except in very thin layers, the most concentrated solutions were completely opaque to light. In very thin layers the most concentrated solution was of a dark red color, similar to that of liquid bromine.

Plate XIV(*a*) will be discussed first. The photographic strip nearest to the numbered scale corresponds to the solution which contained no calcium bromide. The solution of concentration 1.271 has its spectrum shown by the strip adjacent to the spark scale. The depth of cell used was 1.41 cm., in order to obtain a spectrogram comparable with the spectrograms for solutions containing copper chloride and dehydrating agents other than calcium bromide. For this depth, however, it was only possible to photograph the first 6 solutions of the series. The spark line of shortest wave length recorded by the negative for the most dilute solution was at 3466.3. The continuous background ceased, however, at about 0.351 μ. The fifth strip on the negative shows very faint transmission from about 0.477 μ to 0.527 μ.

Plate XIV(*a*) gives correctly the details of this strip at the less refrangible side of 0.527 μ. For the sixth solution the negative shows extremely faint transmission from 0.550 μ to 0.581 μ, at which point the sensitivity of the film ceased.

Plate XIV(*b*) gives the spectrogram obtained with the red sensitive photographic plate of the make used throughout the present work. The depth of the cell was 1.41 cm., the same as for Plate XIV(*a*). The strip next to the comparison scales corresponds to the solution of concentration 1.271, while the strip adjacent to the outside edge of Plate XIV(*b*) was acted upon by light that had passed through the solution which contained the smallest mass of calcium bromide. Each exposure to the light from the glower lasted for 2.5 minutes. The fourth strip of the negative in question, which corresponds to the fifth strip of Plate XIV(*a*), shows that transmission began near 0.500 μ and extended to about 1.618 μ. The strip corresponding to the most concentrated solution of the set of 6 solutions now under discussion, showed rather faint transmission from about 0.543 μ to 0.614 μ, with the maximum of intensity at 0.579 μ. It is evident, therefore, that

Plate XIV(a).

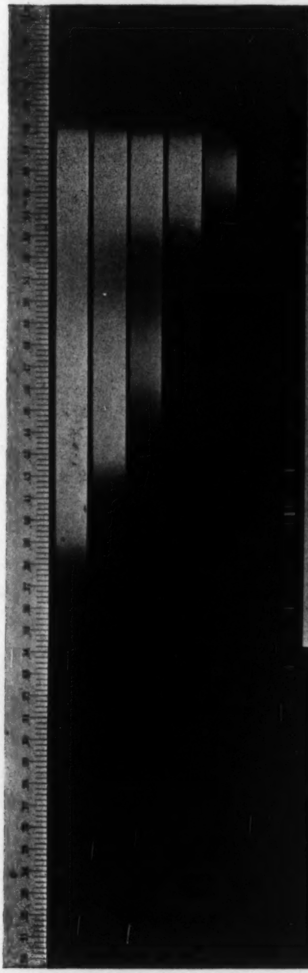


Plate XIV(b).

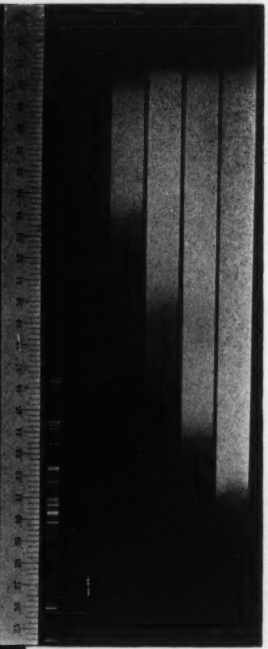


Plate XV(a).

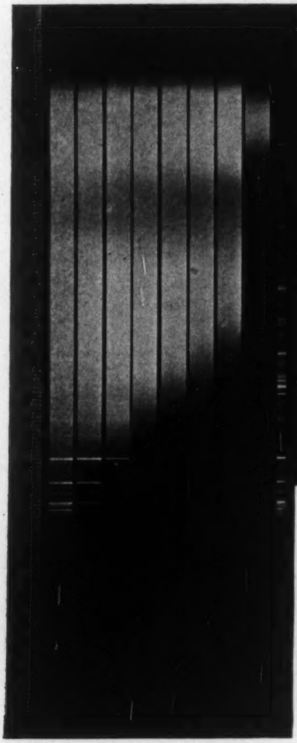
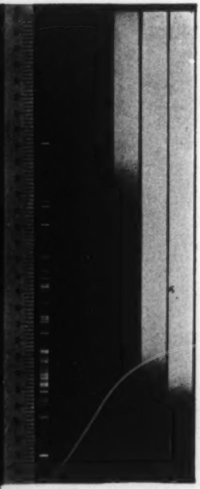


Plate XV(b).



group of 5 solutions, showed that transmission began very weakly near 0.380 μ. It indicated no general absorption in the orange. The third strip, *i. e.*, the one pertaining to the solution of concentration 2.033, showed on the negative that faint transmission began at 0.434 μ, rose to a maximum at 0.462 μ, then faded out to a minimum of almost complete absorption at 0.495 μ and, finally, became strong at about 0.53 μ and so continued to the end of the negative. The fourth strip, which pertained to the solution of concentration 2.542, showed very faint transmission from 0.568 μ to the end of the negative. The negative recorded nothing for the solution of concentration 3.050.

Plate XVI(*a*) gives the absorption of the solution which contained the largest amount of calcium bromide, of concentration 3.804, when placed in the wedge-shaped cell. The liquid prism showed a dark, reddish-brown color. The edge of the spectrogram nearest to the comparison spectrum corresponds, of course, to the least thickness of absorbing layer. The angle of the wedge was about 15′.6 and, therefore, since the cell was adjusted to begin at zero depth, the greatest thickness of absorbing layer was about 0.14 mm. The negative recorded the strong line of wave length 2265.1 as transmitted by the thinnest portions of the solution, but nothing more refrangible. The continuous background did not extend to shorter radiations than 0.233 μ. The ultra-violet absorption is seen to be intense when the very small thickness of the solution is taken into account. The opacity of the solution began to decrease in the neighborhood of 0.346 μ, and rose gradually to a minimum at 4525. The negative recorded the maximum of absorption in the green as at wavelength 0.515 μ. The spectrogram just referred to is supplemented by Plate XVI(*b*). The negative of which this plate is a reproduction was made with a Cramer trichromatic plate. The solution used was the same as for Plate XVI(*a*). The angle of the cell was about 11′.7, and the absorbing layer varied linearally in depth from zero to 0.11 mm. Each of the 3 successive exposures with the Nernst glower had a duration of 2 minutes. The contour of the regions of absorption were es-

Plates XVI(a).

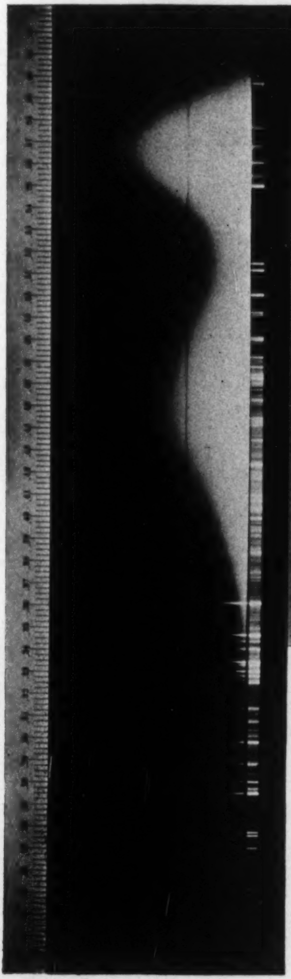
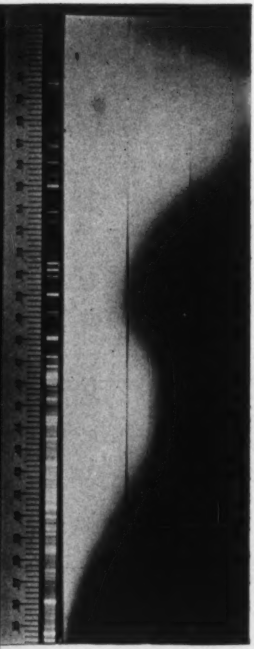


Plate XVI(b).



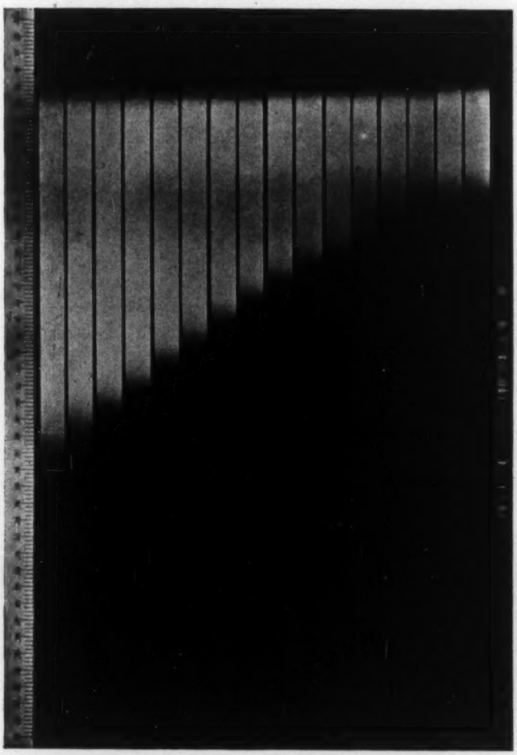
sentially the same as recorded by the negative of Plate XVI(*b*), as by the film of Plate XVI(*a*). Both emulsions gave the wave length 4525 for the more refrangible minimum of absorption. The maximum of absorption for the band in the green was at 0.500 μ, according to the trichromatic plate. Therefore, the 2 spectrograms differed by about 150 A U. in the wave lengths which they give for the absorption band in the green. Since this band is wide and diffuse, it is fair to assign the number 0.508 μ as the approximate position of the middle of the band. Plate XVI(*b*) shows correctly the presence of weak general absorption in the red. The spectrograms for the wedge-shaped layers of solution proved beyond question that the band in the green, as indicated by Plates XIV(*a*), XIV(*b*) and XV(*a*), for the more concentrated solutions, had actual existence and was not due solely to the weak regions of sensibility of the photographic emulsions. The 2 spectrograms of Plates XVI(*a*) and XVI(*b*), by being placed side by side, will illustrate with unusual clearness the part which the photographic plate can play in producing spurious results. This is especially noticeable in the region of the spectrum between 0.55 μ and 0.63 μ.

To serve as a check on the data obtained by the photographic method, as well as for the sake of greater completeness, eye observations were made on the spectra of several of the solutions. The cell with the upper and lower compartments was used, hence the length of the absorbing layer was 2.5 cm. for each solution. The solution of concentration 0.254 of calcium bromide, absorbed the red only a little more than the solution which contained none of this dehydrating agent. These 2 solutions transmitted the yellow and green with equal intensity, at least as far as the eye could tell. The more concentrated solution absorbed almost all the violet, whereas the less concentrated one readily transmitted that color. This accounts for the fact that the former solution appeared bluish green in the cell, whereas the latter had a clear blue tint. The solution of concentration 0.508 absorbed the red just a little more than the one of concentration 0.254. The change was too small to admit of quantitative determination with the dispersion used. For both solutions faint transmission began in the neighborhood of 0.639 μ. The yellow and green are not as bright for the more concentrated solution as for the less concentrated one. Also, the former absorbed considerably more of the blue than the latter. Quantitatively, the same changes were observed when the spectrum of the solution of concentration 0.763 was compared with that of the solution of concentration 0.508. The stronger solution of this pair cut off almost all of the blue and very appreciably weakened the green.

The next solution of the series, of concentration 1.017, absorbed the red a little more than the solution of concentration 0.763. The stronger solution exerted marked general absorption on all the light transmitted, and it absorbed completely all the blue and green as far as the beginning of the yellow-green. If the extreme limits of the regions of transmission for the more concentrated solution be given roughly by 0.630 μ and 0.508 μ, then the corresponding wave lengths for the less concentrated solution would be, respectively, 0.636 μ and 0.468 μ.

The solution which contained the greatest amount of calcium bromide of concentration 3.804, was completely opaque to all visible light in layers of 0.93 depth. A layer 0.12 cm. thick, transmitted, weakly, a narrow band of red extending from about 0.716 μ to 0.653 μ. Red alone was transmitted by a layer of this solution only at 0.06 cm. in thickness. When placed in the wedge-shaped cell, the solution showed very distinctly the 2 bands given by Plates XVI(*a*) and XVI(*b*), *i. e.*, the one in the blue-green and the other in the violet and ultra-violet. So very intense was the absorption of the solution in question, that when a little of it was poured on a plane, parallel piece of quartz, and allowed to drain off with the quartz placed vertically in front of the slit of the spectroscope, the band in the blue-green could be seen distinctly. The results of the freezing point determinations for the solutions which contained copper chloride and calcium bromide are given in Table X. The dark green solu-

Plate XVII.



tions became much lighter in color when they were cooled down in the neighborhood of their freezing points.

The electrical conductivities of the solutions in question were not determined.

Table X.

1. Concentration of $CuCl_2$ in the mixture.	2. Concentration of $CaBr_2$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $CaBr_2$ alone were present.	5. Molecular lowering of freezing-point if $CaBr_2$ alone were present.	6. Molecular lowering of freezing-point for $CaBr_2$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.398	0.000	2°.433	—	—	—	—
“	0.254	4°.250	1°.817	7°.15	5°.22	1°.93
“	0.508	6°.480	4°.047	7°.97	5°.58	2°.39
“	0.763	8°.660	6°.227	8°.16	5°.65	2°.51
“	1.017	11°.325	8°.892	8°.74	6°.40	2°.34
“	1.271	14°.40	11°.97	9°.42	7°.59	1°.83
“	1.525	18°.25	15°.82	10°.37	8°.71	1°.66
“	2.033	28°.0	25°.57	12°.58	10°.42	2°.16
“	2.542	40°.0	37°.57	14°.78	13°.31	1°.47
“	3.050	56°.0	53°.57	17°.56	15°.80	1°.76
“	3.389	?	—	—	—	—

Copper Chloride and Aluminium Chloride. (See Plate XVII, reduced to three-fourths of the original size.) The concentrations of the mother solutions of the copper and aluminium salts were, respectively, 3.976 and 2.75. The several solutions of the series had the following concentrations of aluminium chloride: 0.000, 0.165, 0.330, 0.495, 0.660, 0.825, 0.990, 1.155, 1.320, 1.485, 1.650, 1.815, 1.980, 2.145, 2.310, 2.482. The successive differences in concentration were all equal to 0.165, except the last, which equaled 0.172. The solutions varied in color from pure blue, through various intermediate shades of greenish blue, bluish green, and clear green, to greenish-yellow. The photographic strip next to the numbered scale corresponds to the solution which contained only copper chloride, and the successive strips, of course, became shorter and shorter as the amount of dehydrating agent in the corresponding solutions increased. The depth of the cell was 1.41 cm.

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[1] Interpolated from the table given by Jones and Bassett: THIS JOURNAL, **33**, 550 (1905).

The half-films were not developed simultaneously. The last 2 strips, corresponding to the most concentrated solutions, are not quite comparable with the first 14, as is shown by the fact that they extend a little too far out towards the red end of the spectrum. This was due to opening the slit of the spectrograph a little too widely, as the result of an accidental blow to the micrometer head and the failure to produce exactly the original adjustment.

The negative for the first strip recorded very faintly the intense cadmium line of wave length 3403.7, but nothing more refrangible. The continuous background, however, barely extended to 0.347 μ. According to the negative the most concentrated solution began to transmit at 0.504 μ.

Since the concentrations of the aluminium chloride are in arithmetical progression, the spectrogram shows at a glance the fundamental relation between the limit of absorption of the shorter waves and the concentration of the solution. That the curve of absorption advanced rapidly along the wave lengths at first, and then changed by smaller steps, is shown by the fact that about 150 A. U. lie between the more refrangible ends of the third and fourth photographic strips, whereas only 50 such units are comprised in the corresponding interval between the fifteenth and sixteenth strips.

The solutions were studied in pairs, with the aid of the spectrograph and double-compartment cell. The data obtained visually for the limits of absorption in the violet and blue, agree completely with the photographic results and, therefore, they will not be repeated. Each solution absorbed the red a little more than the one immediately preceding and, hence, the less concentrated member of the set.

The dispersion of the spectroscope was not great enough in this region to enable the observer to obtain quantitative results for consecutive solutions. The most dilute solution began to transmit red at about 0.644 μ, and the most concentrated had, approximately, the same intensity of transmission at 0.629 μ. Therefore, since there were 16 solutions and 15 increments of concentration, the average increase in absorption in the red was 10 A. U. Judged by the eye, the extreme solution of the series transmitted the yellow-green with the same intensity.

The solution of concentration 2.482 of aluminium chloride, was compared with some of the solutions which contained copper chloride and calcium chloride. It was found that the solution having the concentration 3.788 of calcium chloride, had almost identically the same region of transmission as the most concentrated solution of the set containing aluminium chloride.

The cryoscopic data for the solutions which contained the chlorides of aluminium and copper are given below in Table XI:

Table XI.

1. Concentration of $CuCl_2$ in the mixture.	2. Concentration of $AlCl_3$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $AlCl_3$ alone were present.	5. Molecular lowering of freezing point if $AlCl_3$ alone were present.	6. Molecular lowering of freezing point for $AlCl_3$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.398	0.000	2°.433	—	—	—	—
"	0.165	3°.900	1°.467	8°.89	5°.72	3°.17
"	0.330	5°.740	3°.307	10°.02	6°.27	3°.75
"	0.495	7°.850	5°.417	10°.94	7°.02	3°.92
"	0.660	10°.325	7°.892	11°.96	7°.80	4°.16
"	0.825	13°.3	10°.87	13°.18	8°.79	4°.39
"	0.990	17°.0	14°.57	14°.72	9°.92	4°.80
"	1.155	21°.8	19°.37	16°.77	11°.11	5°.66
"	1.320	27°.0	24°.57	18°.61	12°.55	6°.06
"	1.485	32°.5	30°.07	20°.25	14°.04	6°.21
"	1.650	38°.8	36°.37	22°.04	15°.65	6°.39
"	1.815	46°.5	44°.1	24°.30	17°.57	6°.73
"	1.980	55°.5	53°.1	26°.82	19°.50	7°.32
"	2.145	66°.0	63°.6	29°.65	21°.43	8°.22
"	2.310	?	—	—	—	—

The electrical conductivities, together with the corresponding concentrations of the solution containing copper chloride and aluminium chloride, are given in Table XII. The numbers in the second and fourth columns are expressed in reciprocal ohms and reciprocal centimeters:

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[1] Interpolated from the table given by Jones and Getman: Z. physik. Chem., 49, 422 (1904).

Table XII.

Concentration of $AlCl_3$.	Conductivity.	Concentration of $AlCl_3$.	Conductivity.
0.000	0.02996	1.485	0.05917
0.165	0.04264	1.650	0.05504
0.330	0.05312	1.815	0.05028
0.495	0.05834	1.980	0.04584
0.660	0.06150	2.145	0.04054
0.990	0.06366	2.310	0.03486
1.155	0.06400	2.482	0.02924
1.320	0.06273	—	—

The data of the last table are shown graphically by Fig. 13. The abscissae denote concentrations of aluminium chloride, and the ordinate give the corresponding conductivities of the solution. This curve has a marked maximum like all the 4 preceding curves. Moreover, the concentration asso-

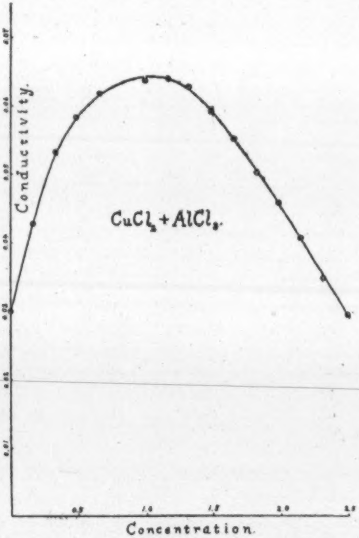


Fig. 13.

ciated with the maximum of conductivity in question, has the value 1.1, and this is exactly the same value as was found for the corresponding point of the curve pertaining to the solutions which contained cobalt chloride and aluminium chloride.

Copper Bromide and Calcium Chloride.—(See Plate XVIII(*a*) and XVIII(*b*), reduced to three-fourths of the original size.) The concentrations of the mother solutions of copper bromide and calcium chloride were, respectively, 2.186 and 4.51. The concentrations of the calcium chloride in the solutions, whose absorption spectra are given by the plates designated above, were: 0.000, 0.451, 0.902, 1.353, 1.804, 2.255, 2.706, 3.157, 3.608 and 4.059. The successive differences in concentration were all equal to 0.451. The concentration of the copper bromide in all the solutions had the constant value 0.219. By transmitted daylight the solutions, in columns 2.5 cm. long, had colors which varied from greenish blue, through various shades of green and brownish green, to dark reddish brown. The photographic strip nearest to the number scale of Plate XVIII(*a*) corresponds to the solution which contained only the one salt. The remaining strips succeed one another in the order of increasing amounts of calcium chloride in the solutions, so that the strip adjacent to the comparison spectrum pertains to the solution of concentration 0.059. The depth of the cell was 1.41 cm. The times of exposure for the Nernst glower and spark were, respectively, 90 seconds and 80 seconds. The line of demarkation of the half-films lies between the fifth and sixth photographic strips, counting either way.

Of the various facts brought out by the negative for Plate XVIII(*a*), the following are the more striking: In the most dilute solution transmission began at 0.377 μ, the second photographic strip began at 0.382 μ. On the negative the fourth and fifth strips commenced at about 0.419 μ and 0.499 μ, respectively. Consequently, when the concentration of the calcium chloride was changed from 0.000 to 0.451, the end of the absorption band in the ultra-violet and violet was displaced towards the red by 50 A. U. Again, when the concentration of the dehydrating agent varied from 1.353 to 1.804, the above-mentioned end of the absorption band was displaced by 300 A. U. in the same direction. Therefore, as is easily seen from the spectrogram, up to a certain concentration the end of the band encroached more rapidly on the region of longer waves, as the concentration of calcium chloride increased. In all the cases discussed in the preceding pages, the successive increments of absorption decreased steadily as the concentration of the dehydrating agent increased in arithmetical progression. As just noted, the change is exactly the reverse for the solutions of copper bromide and calcium chloride. With the sixth photographic strip the end of the absorption band altered somewhat its nature. The negative showed that very weak transmission began at about 0.478 μ, and extended over a relatively wide range of wave lengths. In fact, comparatively intense transmission began only near 0.528 μ. The negative strip corresponding to the most concentrated solution showed that transmission was weak and began in the neighborhood of 0.522 μ.

The negative of which Plate XVIII(*b*) is a reproduction, was taken with a Cramer trichromatic plate. The photographic strip adjacent to the scales corresponds to the most concentrated solution of the set, and the strip at the opposite side of the spectrogram corresponds to the solution of concentration 2.55. The depth of the cell was 1.41 cm. Each exposure to the light from the Nernst filament was 2 minutes in length. The negative strip last mentioned showed that faint transmission began near 0.485 μ, and continued weak to about 0.494 μ. The apparent lack of agreement between the sixth strip of Plate XVIII(*a*) and the fifth strip of Plate XVIII(*b*), is due as much to the difference in length of the respective exposures as to the peculiarities of the photographic emulsion. Plate XVIII(*b*) recorded the beginning of transmission as at wave length 0.552 and this is exactly the same as was obtained from the negative of Plate XVIII(*a*).

Eye observations were made on the solutions in pairs, with the aid of the two-compartment cell. The results obtained

Plate XVIII(a).

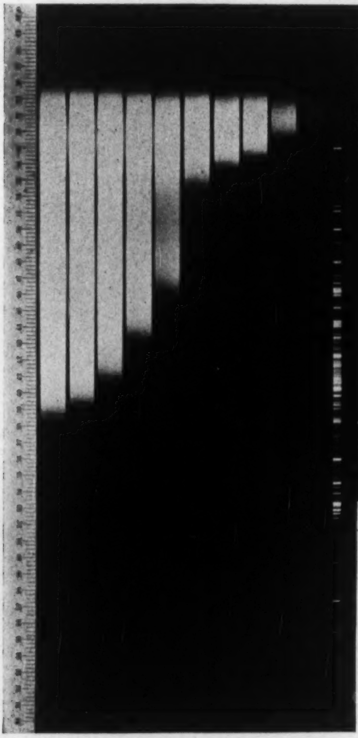
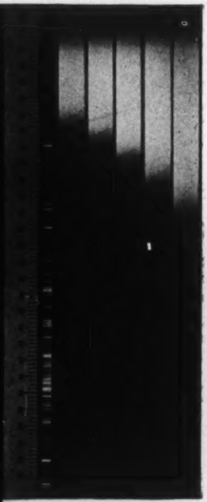


Plate XVIII(b).



by the spectroscope confirmed in detail those derived from the negative. It was noted, especially, that the successive increments of absorption of the band in the violet at first increased with the like change in concentration, and then decreased for the most concentrated solutions. The band in the red extended to the shorter wave lengths by such small increments, when the passage from one solution to its more concentrated successor was made, that it was only possible to obtain the average value of this displacement. Transmission of equal intensity for the most concentrated solution, and for the one which contained no calcium chloride, began at 0.647 μ and 0.667 μ, respectively. Since there were 9 differences in concentration, the average value of the shift of the end of the band in the red was about 22 A. U. When the spectrum of the most dilute solution was compared with that of distilled water, it was observed that the former lacked the deep red and the bright red, and began in the orange-red. These 2 spectra, in the order named, appeared to commence, respectively, at 0.663 μ and 0.772 μ.

The freezing point lowerings of the solutions containing copper bromide and calcium chloride are given in Table XIII:

Table XIII.

1. Concentration of $CuBr_2$ in the mixture.	2. Concentration of $CaCl_2$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $CaCl_2$ alone were present.	5. Molecular lowering of freezing point if $CaCl_2$ alone were present.	6. Molecular lowering of freezing point for $CaCl_2$ in H_2O[1] alone.	7. Column 5 minus column 6.
0.219	0.000	1°.200	—	—	—	—
"	0.451	4°.090	2°.890	6°.41	5°.20	1°.21
"	0.902	7°.620	6°.420	7°.12	6°.12	1°.00
"	1.353	11°.70	10°.50	7°.76	7°.18	0°.58
"	1.804	16°.95	15°.75	8°.73	8°.38	0°.35
"	2.255	24°.5	23°.3	10°.33	10°.03	0°.30
"	2.706	33°.5	32°.3	11°.94	11°.70	0°.24
"	3.157	45°.7	44°.5	14°.10	13°.89	0°.21
"	3.608	58°.(?)	—	—	—	—

The solution of concentration 3.157 changed from reddish brown at room temperature, to greenish yellow in the neighborhood of its freezing point. Salts separated out at about 58° for the solution which had the concentration 3.608 and, consequently, the freezing point lowering could not be determined.

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[1] Interpolated from the results of Jones and Bassett: This Journal, 33, 546 (1905).

Copper Bromide and Calcium Bromide.—(See Plates VII(*a*), XIX(*a*), XIX(*b*), XX(*a*) and XX(*b*); the first 3 are reduced to three-fourths of the original size). The concentrations of the mother solutions of copper bromide and of calcium bromide were, respectively, 2.186 and 4.236. The constant concentration of the copper salt in all of the solutions was 0.219. The concentrations of the calcium bromide were 0.000, 0.254, 0.508, 0.762, 1.017, 1.271, 1.525, 1.779, 2.033, 2.287, 2.542, 2.796, 3.050, 3.304, 3.588 and 3.807. All of the successive differences of concentration were equal to 0.2542, except the last one, which had the value 0.249.

The most pronounced colors of these solutions, in the order of increasing concentration of the dehydrating agent, were light blue, bluish green, green, yellowish green, brownish green and dull brown.

The spectrogram of Plate VII(*a*) will be discussed first. The negatives were taken on Cramer trichromatic plates. The photographic strip adjacent to the scales corresponds to the seventh solution of the series, *i. e.*, to the solution which had the concentration 1.525. The depth of the cell was 1.41 cm. Each exposure to light from the glower was 2.25 minutes in length. A spark exposure of 1.5 minutes was given for each one of the strips which pertained to the 3 most dilute solutions of the set. The negative strip for the solution which did not contain any calcium bromide, recorded the beginning of faint transmission at 0.373. The strip pertaining to the solution of concentration 1.107, showed that transmission began at 0.436 μ and continued to be weak to about 0.520 μ. Transmission was strong from 0.520 μ to the end of the negative.

The darkening of the next negative strip commenced exceedingly faintly at about 0.504 μ, and became very gradually more intense. The strip associated with the solution of concentration 1.525, showed extremely weak transmission from 0.664 μ to the end of the plate, the maximum being at 5875.

Plate XIX(a).

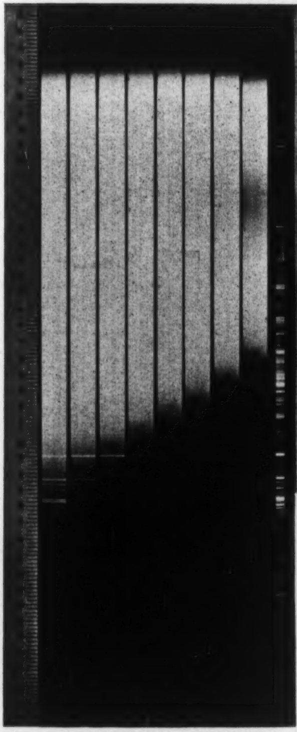
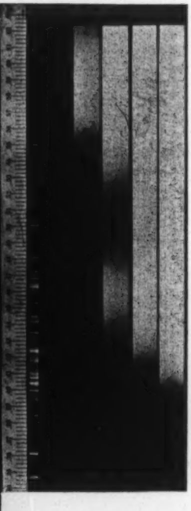


Plate XIX(b).

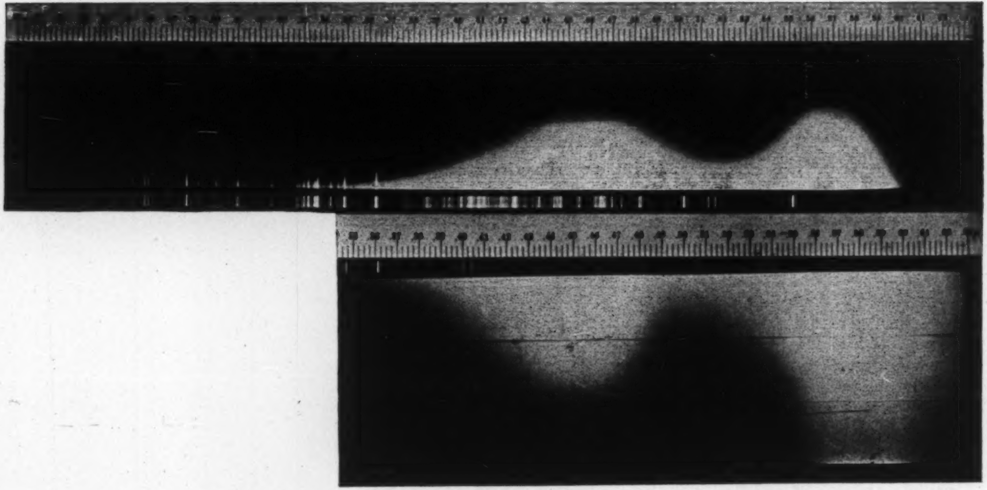


The facts presented by the negative of which Plate XIX(*a*) is a reproduction, will now be considered. The first 8 solutions of the complete series were photographed. The depth of the cell was 0.06 cm. and, therefore, the solutions, when in the cell, showed practically no color. The strips contiguous to the numbered scale and to the comparison spectrum correspond, respectively, to the solutions of concentration 0.000 and 1.779 of the dehydrating agent. The strip pertaining to the most dilute solution recorded the very faintest trace of the air line at 3007.0; the continuous background, however, ceased near 0.308 μ. The negative strip, corresponding to the eighth solution, showed that transmission began near 0.400. When due allowance is made for the known disturbing influences, the 8 strips of Plate XIX(*a*) seem to show that the end of the ultra-violet absorption band shifted in direct proportion to the increments of concentration of the calcium bromide.

It is now desirable to give the most salient points relative to Plate XIX(*b*). The negative of the spectrogram in question was made with a Cramer trichromatic plate. The seventh to the eleventh solutions, inclusive, had their spectra recorded by this plate. The strips pertaining to the solutions of concentration 1.525 and 2.542 are, respectively, nearest to the outside edge of Plate XIX(*b*) and to the scale. The depth of the cell was 0.06 cm. The duration of each exposure to the radiation of the filament was 2.25 minutes. Hence, the seventh and eighth solutions of the complete series have their absorption spectra given by both Plates XIX(*a*) and XIX(*b*). The negative strip, corresponding to solution of concentration 1.525, showed that transmission began at 0.383 μ. The third strip, counting from the outer edge of Plate XIX(*b*), recorded 0.417 μ for the beginning of transmission, and 0.500 μ for the middle of the region of rather weak transmission. The fourth strip showed very weak transmission from 0.436 μ to 0.484 μ, then apparent absorption from 0.484 μ to about 0.530 μ and, finally, stronger transmission from 0.530 μ to the end of the spectrogram. The negative strip pertaining to the solution of concentration 2.542 recorded very weak transmission from 0.555 μ to the end of the plate.

The most concentrated solution of the set was so opaque to light, that its absorption spectrum could only be satisfactorily recorded by the aid of the wedge-cell. For Plate XX(*a*) the angle of the liquid wedge was about 11′.7 and the depth of the absorbing layer increased linearally from zero to 0.11 mm. In the cell the solution appeared to be deep red. The absorption band in the blue-green could be distinctly seen with the aid of the eye-piece. The edges of this band are very diffuse and poorly defined. Obviously, the edge of the negative closest to the comparison spectrum was produced by the light that passed through the least depth of the solution, *i. e.*, nearest to the refractive edge of the liquid prism. Even for the thinnest layers the continuous background was completely absorbed from 0.200 μ to about 0.240 μ. The negative showed that the absorption began to decrease in the vicinity of 0.335 μ, and continued to do so according to a curve of gentle slope until it reached a minimum at 0.455 μ. From this point on, the absorption increased to a maximum near 0.517 μ, and then diminished again at the less refrangible side of the absorption band.

Except in so far as the wave length of the middle of the absorption band in the green is concerned, Plate XX(*b*), whose negative was taken with a Cramer trichromatic plate, fully confirms the facts as recorded by the spectrogram of Plate XX(*a*). The angle of the wedge was only 7′.8, and since the least depth was zero, the greatest depth of absorbing layer was about 0.08 cm. The 3 successive exposures to the light from the glower were each given 2.25 minutes. The negative was somewhat underdeveloped. It gave, for the first maximum of transmission, the wave length 0.454 μ. The maximum of absorption, but not the center of the band in the green, was recorded as 0.500 μ. The spectrogram of Plate XIX(*b*) gives a more correct graphical representation of the band in the blue-green than does that of Plate XIX(*a*). The asymmetry of this band, and its greater width of penumbra on the less refrangible side, was confirmed directly by observations.



Plates XX(a) and XX(b).

The results obtained by a rather extended series of eye observations, on the solutions which contained copper bromide and calcium bromide will now be given in some detail.

The solutions were first studied in pairs by the aid of the double compartment cell. The length of each absorbing column was, therefore, 2.5 cm. As the solutions became more and more concentrated, the band in the red gradually shifted its visible boundary to shorter wave lengths. The increments of absorption in the violet and blue appeared to become greater and greater as the more and more concentrated solutions were studied. The solution of concentration 1.107 of calcium bromide absorbed the blue-green and blue almost completely, and also dimmed the entire region of transmission appreciably more than the next less concentrated solution. In like manner, the solution of concentration 1.271, showed throughout weaker transmission than the next lower member of the series, and it absorbed completely all colors more refrangible than the green. In addition, this color was greatly weakened in intensity. The last 2 solutions just mentioned showed, at the more refrangible side of the green, a fairly long region of transmission, which was so extremely faint that the eye could not detect any color as such, but only an indefinite gray. The spectrum of the solution whose concentration was 0.254 was compared with that of distilled water. Very weak transmission of the same intensity began at 0.665 μ and 0.770 μ, respectively, for the solution and for the pure water. The solution also absorbed the extreme violet quite noticeably.

In order to study with the spectroscope the solutions of greater concentration that 1.525, as well as to obtain checks on the data secured photographically, the cell sketched in Fig. 3 was adjusted to a depth of 0.06 cm., and arranged so as to be used with its axis of figure horizontally. The following facts were then observed and noted: In this cell the solution of concentration 2.033 had a light yellowish brown color. The spectrum extended from about 0.747 μ to 0.425 μ. The weakening of transmission in blue-green was very delicate.

The spectrum transmitted by the solution of concentration 2.287 began about 0.740 μ, and continued to be uniformly bright to, say, 0.540 μ. At this wave length the penumbra of the absorption band in the blue-green commenced. The maximum of absorption appeared to have the position given by 0.500 μ. This absorption was not complete, since a little light could be seen at all points of the band, not excepting the maximum. Beyond this band transmission rose to a maximum near 0.465 μ, and then faded away to nothing in the vicinity of 0.435 μ. The numbers given for the extreme limits of transmission are, obviously, not very accurate, and are merely intended to suggest the positions of these boundaries. The spectrum of the next solution in order of concentration, 2.542, was, apparently, more complex than that of any other solution of the series. Transmission began at 0.737 μ, rose to a maximum at 0.652 μ and then increased in intensity to 0.603 μ. From this point to about 0.545 μ, the brightness of the spectrum seemed to remain constant, but much less bright than at the wave length 0.652 μ. A definite absorption band, whose middle was approximately at 0.508 μ, began near 0.545 μ. Beyond this band transmission rose to a maximum at 0.465 μ, and then gradually faded out to zero value in the neighborhood of 0.445 μ.

The transmission spectra of the solutions just discussed were comparatively bright, and extended over relatively wide regions of wave lengths, while the spectra to be described below were less intense and much prescribed. In other words, the transition was rather abrupt.

The solution of concentration 2.796 began to be transparent at 0.735 μ. The spectrum rose to a maximum of intensity near 0.657 μ, and then gradually fell off to small intensity at 0.600 μ. Transmission was pretty uniform between 0.600 μ and 0.550 μ. At the latter wave length the light decreased abruptly to zero. There was no visible return of transmission in the region of the shorter waves.

Transmission began at 0.730 μ, rose to a maximum at 0.660 μ, and decreased to almost no color near 0.590 μ, for the solution of concentration 3.050. An extremely weak region of transmission extended from a little beyond 0.590 μ to 0.575 μ. Because of its faintness, the subjective color throughout this region was gray.

The solution of concentration 3.304 transmitted chiefly bright red. The extreme limits of the spectrum were, approximately, 0.733 μ and 0.625 μ, the brightest spot being at 0.670 μ. Only red from about 0.730 μ to 0.640 μ was transmitted by the solution of concentration 3.558. Finally, the most concentrated solution of the series transmitted red from about 0.725 μ to 0.650 μ. The most intense portion of this spectrum was near 0.680 μ.

The lowerings of the freezing point of water produced by the solutions which contained copper bromide and calcium bromide are given below in Table XIV.

Table XIV.

1. Concentration of $CuBr_2$ in the mixture.	2. Concentration of $CaBr_2$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $CaBr_2$ alone were present.	5. Molecular lowering of freezing point if $CaBr_2$ alone were present.	6. Molecular lowering of freezing point for $CaBr_2$ in H_2O[1] alone.	7. Column 5 minus column 6.
0.219	0.000	1°.200	—	—	—	—
"	0.254	2°.836	1°.636	6°.44	5°.22	1°.22
"	0.508	4°.550	3°.350	6°.59	5°.58	1°.01
"	0.762	6°.696	5°.496	7°.21	5°.76	1°.45
"	1.017	9°.075	7°.875	7°.74	6°.40	1°.34
"	1.271	11°.90	10°.70	8°.42	7°.75	0°.67
"	1.525	15°.35	14°.15	9°.28	8°.71	0°.57
"	1.779	19°.5	18°.3	10°.29	9°.03	1°.26
"	2.033	24°.0	22°.8	11°.21	10°.42	0°.79
"	2.287	29°.5	28°.3	12°.37	11°.93	0°.44
"	2.542	36°.0	34°.8	13°.69	13°.31	0°.38
"	2.796	43°.5	42°.3	15°.13	14°.56	0°.57
"	3.050	52°.4	51°.2	16°.79	15°.80	0°.99
"	3.304	66°.5	65°.3	19°.76	17°.05	2°.71
"	3.558	?				

The solution of concentration 3.558 could not be frozen within the range of the scale of the thermometer, *i. e.*, between 0° and —80°.

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[1] Interpolated from the results of Jones and Bassett: THIS JOURNAL, **33**, 550 (1905).

Copper Bromide and Aluminium Chloride.—(See Plates XXI(*a*) and XXI(*b*), both reduced to three-fourths of the original size.) The concentrations of the mother solutions of copper bromide and aluminium chloride were, respectively, 2.186 and 2.75. In the series of solutions discussed below, the constant concentration of the copper salt was 0.219. The concentrations of the dehydrating agent were 0.000, 0.275, 0.550, 0.825, 1.100, 1.375, 1.650, 1.925, 2.200 and 2.480. All the successive differences in concentration are equal to 0.275, except the last increment, which equals 0.280. As the amount of the dehydrating agent increased, the solutions changed from greenish blue to brown, passing through various intermediate shades of bluish green, green, olive and brownish green. The photographic strips corresponding, respectively, to the solutions which contained none of the aluminium chloride, and the greatest amount of this salt, are adjacent to the numbered scale and to the comparison spectrum. The depth of the cell was 1.41 cm. The most noticeable facts shown by the negative of Plate XXI. are the following:

The faintest trace of the intense cadmium doublet at 3612 was recorded by the strip corresponding to the aqueous solution which contained only copper bromide. The continuous background, however, faded out at about 0.371 μ. The spectrogram shows very clearly that for the first 7 or 8 solutions the absorption band, which included the entire ultraviolet region, advanced by ever-increasing increments as the concentration of the aluminium chloride became greater and greater. The seventh negative strip showed that transmission began at 0.502, and increased very gradually to about 0.527. From this point on, the solution was quite transparent. The strip corresponding to the most concentrated solution recorded relatively weak transmission of the less refrangible parts of the spectrum than 0.554 μ.

The negative, of which Plate XXI(*b*) is a reproduction, was taken with a Cramer trichromatic plate. The photographic strips correspond to the 5 more concentrated solutions of the complete set of 10. Obviously, the strip nearest to the scale pertains to the solution that contained the

Plate XXI(a).

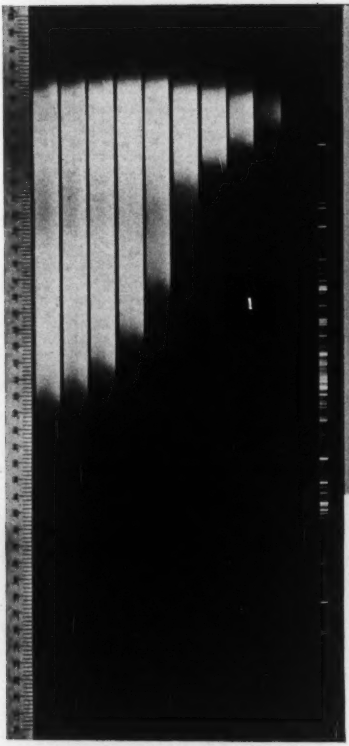

Plate XXI(b).

greatest amount of aluminium chloride. The depth of the cell was here also 1.41 cm. The time of exposure for the Nernst glower was 2 minutes. The strip corresponding to the solution of concentration 1.375, showed that transmission began weakly at 0.473 μ, approached gradually its full value, and continued complete nearly to the end of the plate. The photographic record began at about 0.552 μ for the strip pertaining to the most concentrated solution. The general outline suggested by the ends of photographic strips of Plate XXI(*b*), which ends show the beginning of transmission, curves in a direction exactly opposite to that of the contour outlined by the first 5 strips of Plate XXI(*a*). In other words, for the more concentrated solution in series, the successive increments of absorption decreased as the concentration of the aluminium chloride increased. By means of the two-compartment cell, eye observations were made on the solutions in pairs. The results obtained photographically were confirmed in all respects. One of the most important facts noted was that, as the concentration of the dehydrating agent increased in arithmetical progression, the successive increments of the absorption region which comprised the ultra-violet, first increased, and then subsequently decreased. Stated otherwise, the curve of absorption apparently possessed a point of inflection. The existence of the comparatively long region of weak transmission of the green for the sixth solution, was established visually as well as photographically. As far as the red end of the spectrum was concerned, every solution absorbed the red a little more than the next less concentrated member of the series. It was only possible to obtain a value for the mean displacement of the red or orange end of the spectrum. For the aqueous solution which contained only copper bromide, and for the most concentrated member of the set, transmission of about the same intensity began, respectively, at 0.670 μ and at 0.645 μ. Therefore, since there were 10 solutions in the series, the average displacement of the red end of the spectrum was 10 A. U.

The lowerings of the freezing point of water, produced by the solutions which contained copper bromide and aluminium chloride, are recorded below in Table XV.:

Table XV.

1. Concentration of $CuBr_2$ in the mixture.	2. Concentration of $AlCl_3$ in the mixture.	3. Observed freezing point lowering of the mixture.	4. Lowering of freezing point if $AlCl_3$ alone were present.	5. Molecular lowering of freezing point if $AlCl_3$ alone were present.	6. Molecular lowering of freezing point for $AlCl_3$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.219	0.000	1°.200	—	—	—	—
"	0.275	3°.538	2°.338	8°.50	6°.05	2°.45
"	0.550	6°.900	5°.700	10°.36	7°.30	3°.06
"	0.825	11°.20	10°.00	12°.12	8°.79	3°.33
"	1.100	17°.1	15°.9	14°.45	10°.71	3°.74
"	1.375	25°.5	24°.3	17°.67	13°.06	4°.61
"	1.650	36°.0	34°.8	21°.09	15°.65	5°.44
"	1.925	51°.0	49°.8	25°.87	22°.07	3°.80
"	2.200	?				

The solution of concentration 1.925 changed from reddish brown to pea-green, as the temperature fell from room value to the neighborhood of —50°. On account of excessive undercooling it was not possible to freeze with a mixture of ethyl alcohol and solid carbon dioxide the solution of concentration 2.200. This solution became a light green, very viscous jelly at —75°.

GENERAL SUMMARY OF RESULTS.

Discussion of the Several Theories.—The theory of Engel, that the blue color of solutions of cobalt chloride is due to the presence of double salts, appears to us untenable for a number of reasons: In the first place, it has been shown by Jones and Ota[2] and Jones and Knight[3] that double chlorides, in general, even in very concentrated solutions, are largely broken down into the single salts, which are dissociated in the usual manner. In such solutions we should not have simply the molecules of the double salt, but a large number of the ions resulting from the dissociation of such a compound.

Again, this theory is entirely out of accord with the fact that a strong aqueous solution becomes blue when heated. The increase in the hydrolysis with the comparatively slight rise in temperature, is not sufficient to liberate enough hydrochloric acid to account for this color change on the basis of a compound being formed with this acid.

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[1] Interpolated from the results of Jones and Getman: Z. physik. Chem., **49**, 422 (1904).

[2] THIS JOURNAL, **22**, 5 (1899).

[3] *Ibid.*, **22**, 110 (1899).

Further, this theory is not in accord with the color changes which manifest themselves when water is added to solutions of cobalt chloride, etc., in methyl and ethyl alcohols and acetone, where no double salt can be present.

The following consideration would appear to have very direct bearing upon the theory under discussion: An examination of the spectrograms will show that, with increasing amount of the dehydrating agent or salt, the absorption bands widen. With increasing amounts of the dehydrating agents used in this work, more and more of the double halides, if they existed, would be formed, since the solutions would be more and more concentrated. This would mean that the vibrating, charged particle was becoming more and more complex. The above facts are not in harmony with one another. The most probable interpretation of the widening of the absorption bands with increase of concentration is, that the vibrating, charged particle is becoming of smaller and smaller mass, and can thus vibrate in resonance with a larger number of periods.

There are also a number of objections to the theory proposed by Ostwald to account for the color changes of cobalt chloride. It will be recalled that Ostwald takes the view that the blue color is due to the cobalt molecule, and the red color to the cobalt ion. This would not account for the great color change produced by warming a concentrated, aqueous solution of cobalt chloride. The dissociation would decrease a very small amount for the change in temperature from, say, 25° to 75° or 80°, as is shown by the work of Jones and West,[1] and especially by that of Noyes and Coolidge.[2] This slight change in the dissociation would be entirely incapable of accounting for the marked color changes produced. Further, the amount of hydrochloric acid liberated as the result of the increased hydrolysis with rise in temperature, would be far too small to drive back the dissociation sufficiently to produce such marked changes in color.

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[1] THIS JOURNAL, 34, 357 (1905).

[2] Z. physik. Chem., 46, 323 (1903).

Another objection to this view is that the quantity of water required to color a blue alcoholic solution red, is altogether too small to produce a sufficient increase in the dissociation to cause the observed color change.

Further, the amount of water that is required to change very appreciably the color of a solution of cobalt chloride, rendered blue by the presence of aluminium chloride, is very small indeed, as is shown by Table VII. This small quantity of water could not, of course, materially increase the dissociation of the solution of cobalt chloride.

This shows that we cannot account for the color changes solely, or even chiefly, on the basis of dissociation.

That there are, apparently, insurmountable objections to the theory of Donnan and Bassett, that the blue color is due to complex ions of cobalt, is made evident by the following considerations:

The alcoholic solutions show, in general, the same color changes when water is added, as are manifested by the aqueous solutions in the presence of dehydrating agents. A comparison of the spectrograms in this paper, and the eye observations, with those in the paper immediately following this one, will show that the same absorption bands appear in the aqueous and in the non-aqueous solutions. These bands, however, undergo the well-known shift in position, due to a change in the dielectric constant of the medium produced by the presence of more and more of the dehydrating agent. It is, at least, very doubtful whether we should have the same ionic complexes in the non-aqueous solutions as in the solutions in water as the solvent.

Having pointed out the most serious defects in the various theories that have been proposed to account for such color changes as have been dealt with in this paper, we shall proceed to show how all the facts recorded in the preceding pages confirm the hydrate theory in the form emphasized by Jones.

Since the relation between the selective absorption of light and the existence of hydrates, may not be obvious, a brief discussion of this matter will now be given. Of course, in the present stage of our knowledge of the nature of solutions, it is not possible to form a detailed mechanical conception of the various processes which come into play in solutions, when arbitrary changes are made in concentration, in the temperature, in the solvent, etc. Nevertheless, the general view which we hold may be explained as follows: In the first place, *the phenomenon of absorption is, primarily, one of resonance,* and since light waves are electromagnetic waves, it follows that the absorbing system must be electrical in its nature. The *energy of a vibration of a given period will be absorbed to the greatest extent by a system whose natural period of vibration is most nearly equal to that of the first vibration,* and it may not be absorbed at all by a system whose period differs appreciably from that of the incident waves. In this way the selective phase of the phenomenon of absorption is explained. It is almost superfluous to state that the resonator, of which we are conceiving, may be very complex, and may have any finite number of discrete periods of vibration. Exactly how this resonator is related to the ion of electrolysis, as this term is usually understood, cannot be decided at present. Nor is this relationship a matter of fundamental importance to the question of the existence or non-existence of hydrates. It seems natural to suppose that the vibrations of this resonator would be strongly influenced by the nature of the medium surrounding it, not only by virtue of changes in the viscosity, specific inductive capacity, etc., of the medium, but also by the condensation around, or near it, of complexes of water molecules. The way in which these complexes or hydrates might affect the absorption of the resonator is as follows: The vibration of a given period of the resonator might be so greatly damped, either directly or indirectly, by the hydrate, that its amplitude would fall below the value which marks the limit of our experimental means of detecting absorption.

If this were the case we should not be aware of the existence of the absorption, and we should, therefore, say that no absorption of the given period takes place. In fact, when we say that pure water is transparent to light of one given period, for example, the D_3 line of helium, we do not mean that the absorption is absolutely zero, with mathematical exactness, but we do mean that it is, perhaps, indefinitely less than we can detect experimentally. Doubtless, if a column of absolutely pure water of sufficient length could be obtained, it would be found that the region of absorption for the Schumann waves would widen out simultaneously with the bands in the infra-red, until the entire visible spectrum would be dimmed by general absorption. The next question is, how should we expect the hydrates to affect the width of a given absorption band, or a limit of a region of absorption. The maximum of absorption of a band would correspond to that vibration of the resonator which was the least damped, and which, therefore, had the greatest amplitude; whereas the penumbra at the boundary of the band would correspond to those vibrations of the resonator which were damped to a great degree, and which, therefore, had very small amplitude. It has been tacitly assumed that the incident radiation was continuous, and practically comprised all of the periods of the resonating system. *If, now, the hydrate associated with a given resonator increased in mass by the addition of water, it would, of course, damp the vibrations more and more, and thus, by decreasing the amplitudes of the penumbral vibrations, cause the band to become narrower and narrower.* That absorption still existed in the region from which it had apparently disappeared, could be shown at once by simply increasing the length of absorbing column, until the penumbra had widened out to its original value, everything else being kept constant. *Conversely, when the extent of hydration decreases, the regions of absorption would widen out and extend over a greater range of periods and wave lengths.* Assuming that the argument advanced above is valid, then it does not seem possible to escape the conclusion that hydrates exist, since the theory accounts so perfectly for the facts. We shall deduce the evidence for this agreement in some detail from the spectrograms and other sources of information.

Plate II. shows that the regon of absorption in the ultra-violet widens out as the concentration of the cobalt chloride increases. The same fact is shown in Plates II and III(*a*), by the absorption band in the green. *As the concentration increases, the relative amount of water at the disposal of one cobalt system decreases, and, therefore, in accordance with the preceding theory, the band must become wider.*

The same phenomenon in the ultra-violet is shown by Plate V., for the solutions of copper chloride in water. Plate III(*b*) also brings out the facts for the band in the red.

It is obvious that in interpreting the spectrograms, the difference between the observed widening of the absorption bands, and the widening which would have theoretically been produced if a change in concentration had meant nothing more than an increase in the number of absorbing particles per unit volume, and not a change in their effective mass, had to be taken into account.

The well-known theoretical formula involving the laws of Beer and Lambert is $I = I_0 a^{dc}$, where d symbolizes the thickness of absorbing layer and c denotes the concentration. The remaining symbols have obvious definitions.

Further details concerning these laws may be found in the third volume of Kayser's "Handbuch der Spectroscopie," pp. 20, 25 and Chap. II. E.

Plates III(*c*) and VI. show conclusively the widening of the bands with increasing concentration, in the case of aqueous solutions of copper bromide. The data obtained from eye observations on the bands in the red confirm completely the spectrographic results.

Plates VIII., IX(*a*), IX(*b*) and XII. show that the bands in the ultra-violet and green widen out as the amount of calcium chloride in the aqueous solutions of cobalt chloride increases. It will be remembered that in these solutions the *mass of cobalt chloride was kept constant*, while the quantity of the dehydrating agent was varied. These facts agree perfectly with the theory, since the quantity of calcium chloride used has a much greater power to combine with water particles than the cobalt system has. Therefore, as the *concentration of* *the calcium chloride increases, more and more water is taken away from the cobalt chloride, so that the vibrations of the latter are less damped than before, and thus the absorption bands cover a wide range of period.*

The same phenomenon is shown by Plates XI(*a*) and XII. for the solutions containing variable amounts of aluminium chloride and a constant quantity of cobalt chloride.

The progress of the ultra-violet region of absorption, as the quantity of calcium chloride in the solutions containing a constant amount of copper chloride is increased, is very clearly shown by Plate XIII.

Plate XVII. brings out the same facts for the solutions having a constant mass of copper chloride and a variable quantity of aluminium chloride.

The absorption bands of solutions of copper bromide, which differ only in the amounts of calcium bromide contained in the solutions, extend over wider ranges of wave lengths as the percentage of the dehydrating agent increases. This is shown by Plates VII(*a*), XIX(*a*) and XIX(*b*).

The results of eye observations agree in detail with the facts derived from the photographic negatives. See especially Plates VIII(*a*), VIII(*b*), VIII(*c*) and VIII(*d*). When to solutions containing constant amounts of cobalt chloride, or of copper chloride, varying quantities of calcium bromide are added, the absorption phenomena are, in general, more complicated than in the cases just discussed, because of the effective formation, respectively, of cobalt bromide and of copper bromide. Similar conditions arise, of course, when either calcium chloride or aluminium chloride is added to solutions containing a constant amount of copper bromide. A careful study of the negatives corresponding to the mixed solutions of the kind just described, shows that the absorption bands of these solutions conform perfectly to the theory in question, and do not present any exceptions. Earlier investigations have shown that aluminium chloride is a stronger dehydrating agent than calcium chloride. This being the case, we should expect to find that a *given widening of an absorption band of a colored salt, so-called, which* *widening had been caused by the addition of a certain amount of calcium chloride, would be produced by a smaller amount of aluminium chloride.*

Consider the case of cobalt chloride with the other two chlorides just mentioned. See Plates IX(*b*), XI(*a*) and, especially, Plate XII. The pairs of solutions were made up so as to have the same colors when viewed in their bottles. The successive widths of the absorption band in the green, for the solutions which contained calcium chloride, are slightly, but only slightly wider than those of the band of the corresponding solutions of the aluminium chloride series. On the contrary, the concentrations of the calcium chloride were much greater than the concentrations of the aluminium chloride, everything else being kept constant. The concentrations are compared in Table XVI.:

Table XVI.

$CaCl_2$.	$AlCl_3$.
1.676	1.118
2.091	1.394
2.515	1.676
2.671	1.781
2.830	1.887
3.143	2.100
3.555	2.370

The region of absorption in the ultra-violet is not relevant, because of the intense absorption of the short waves by aluminium chloride alone.

Another illustration is afforded by the solutions of copper chloride, together with the chlorides of calcium and aluminium (see Plates XIII. and XVII.). A careful comparison of the negatives shows that the absorption produced by the most concentrated solution of aluminium chloride certainly extended farther into the visible spectrum than the corresponding band for the solution of calcium chloride, which was the third from the end of its series. The concentrations of the calcium and aluminium salts were, respectively, 3.518 and 2.482. The same fact may be brought out very sharply as follows: The two concentrations for the calcium chloride series, which come nearest to the concentration of the strongest aluminium chloride solution, and between which the latter concentration falls, are 2.435 and 2.706. The photographic strips pertaining to the calcium chloride solutions are the tenth and eleventh of Plate XIII., counting from the numbered scale towards the comparison spectrum. A single glance shows that both of these bands of transmission extend to much shorter wave lengths than the last strip of Plate XVII.

That it is, in general, much more difficult to remove the last molecules of water from a given compound than the first, is a well-known fact. Illustrations of this phenomenon are so numerous as to make it almost superfluous to cite specific instances. For all the cases examined, in which only one colored salt was present, and for all the absorption bands that had definite limits and were not accompanied by long regions of weak general absorption, it was found that, as the concentrations of the solutions increased in arithmetical progression, the increments of absorption at one side of the band gradually became less and less. This statement applies both to the solution which contained only one salt, and to those which contained a dehydrating agent together with a colored salt. Since a one-sided region of absorption in the ultra-violet may be looked upon, for the sake of convenience, as the less refrangible side of the band whose center lies beyond 0.200 μ, and hence out in the region of the Schumann waves, and since a one-sided region of absorption in the red is actually the more refrangible side of a band whose centre is situated in the infra-red, the preceding idea may be generalized by saying that the boundaries of all the absorption bands studied were concave towards their respective centers or maxima, as the case may be. The fact that the increments of absorption decreases as the concentration increases, means that the colored system resists the transfer of its associated water molecules to the dehydrating agent, more and more, as the actual number of its associated water molecules becomes less and less. From the standpoint of the colored salt, the process of making up solutions of the same volume, and at the same time increasing the concentration of the salt, is equivalent to taking away some of its molecules of water.

The bearing of this on the decreasing increments of absorption is obvious.

The cases where the spectrograms show that the boundary of the ultra-violet region of absorption was convex towards the shortest wave-lengths, are not really at variance with the preceding explanation, since this convexity is due to either of two causes, or both causes acting simultaneously. One of these conditions is as follows: For a given length of exposure, time of development, color of light, etc., there is an inferior limit of intensity of light, such that, if the intensity falls below this value, the sensitized film or plate will show no darkening even if overdeveloped. Now some of the solutions had very long, weak regions of general absorption at the edge of the ultra-violet region of complete absorption. Also, the intensity of this penumbral companion to the main band increased as the concentrations of the solutions of the series increased, at such a rate as to cause the photographic film to record, apparently, increments of absorption that were too large. In other words, for the more dilute solutions the plate would record the light which was only slightly weakened by the general absorption, as if there were no such absorption at all, and then for the more concentrated solutions it would not give any record of the faint light which passed through the penumbral region. The transition from one condition to the other might be either gradual or, apparently, sudden, according to obvious circumstances. Spurious results of this nature were sometimes corrected by the negative taken on the trichromatic plates, and they were always brought to light by the eye observations with the spectroscope.

The other cause for the apparently anomalous behavior of the contour of the ultra-violet region of absorption, is the gradual superposition of the bands belonging to the 2 colored salts. For example, when calcium chloride was added to the solution containing copper bromide, the absorption is complicated by the production in the solutions of calcium chloride and copper chloride. Of course, the compound absorption spectra of solutions of the kind just mentioned can be distorted by the peculiarities of photographic processes as well as the simpler cases. The well-known color changes which take place when fairly large variations are made in the temperature of the solutions, are in complete agreement with the present theory. For example, when a red solution of red cobalt is sufficiently warmed it becomes blue. As already explained, the blue and red colors correspond, respectively, to wide and narrow bands; or in terms of the theory, to small hydration and to relatively large hydration. But we know, from other lines of evidence, that the complexity of the hydrates decreases with rise in temperature, and thus we have another illustration of the wide applicability of the theory.

When a solution of cobalt chloride has been made deep blue, at room temperature, by the addition of some one of the strong dehydrating agents, it turns red when cooled to the neighborhood of its freezing point. The explanation of this phenomenon, in terms of the theory, is obvious. The corresponding color changes for the copper salts can be explained in exactly the same manner as has been done for cobalt chloride.

Before concluding the discussion of the interpretation of the spectroscopic data, it is desirable to emphasize the fact that all the color changes investigated take place very gradually and continuously, and that there are no sudden variations in the bands and regions of absorption. Perhaps the most striking color change of all is that from blue to green, manifested by copper chloride. The one solution is blue because there is no absorption band in the violet, and yet there is a strong band in the red. The other solution is green because a band has pushed its end out of the ultra-violet into the visible spectrum, and absorbed the violet and, perhaps, weakened the blue.

The band in the red has likewise encroached on the visible spectrum. The apparently abrupt change from blue to green is only due to the fact that the visible spectrum is limited by the sensitivity of the retina to a certain region of wave lengths. If we could see distinctly into the ultra-violet as far as 0.200 μ, we should probably be less hasty in writing about mixtures of the colors of certain ions and molecules. What is meant by the color of an ion? How do absorption bands mix colors?

In conclusion, it is appropriate to call attention to certain facts which were brought out by the present investigation, and which have no direct bearing on the theory of hydrates.

Tables I. and III., for the freezing point lowerings of cobalt chloride, together with either calcium chloride or calcium bromide, show that these solutions change with time. The nature of the change is such as to increase the molecular lowering of the freezing point; in other words, the solutions undergo hydrolysis.

Table VII. shows that the volume of water necessary to change a color of the series in question approximately to that of the next more dilute solution of the set, decreases as the concentration of the first solution increases. The solutions contain cobalt chloride and aluminium chloride.

The reason for the decrease just noted is as follows: When the solutions are very concentrated they contain a relatively small amount of water and, therefore, it requires the addition of only a very small quantity of the latter to change the color of the solution to that of the next lower number of the series. When, on the other hand, the solutions contain a larger amount of water to begin with, it requires a greater quantity than formerly to bring about a definite color change. In other words, the question is one which concerns the ratio of the amount of water added, to the quantity already present, and it does not relate, primarily, to the absolute volume of water concerned. A careful study of the 5 curves for electrical conductivity, shows that the viscosity is chiefly responsible for the decrease in conductivity with increase in the concentration of the dehydrating agent, after a maximum of a curve has been reached. Stated in a slightly different way, the decrease in the velocity of the ions is so much greater than the simultaneous increase in the number of ions, that the conductivity decreases with increase in concentration. The fact that the maxima of the curves for the solutions which contained the same dehydrating agent, occur at approximately the same concentration of this agent, quite independent of the nature of the colored salt in the solution, is due to the relatively small number of ions of the colored salt, as compared with the number of ions of the dehydrating agent. Moreover, as would be expected, the greater the viscosity of the dehydrating agent, the lower the concentration corresponding to the maximum of the curve. Compare, in this connection, the calcium chloride solutions with those of aluminium chloride.

Finally, we wish to express our thanks to the Physical Department for placing at our disposal the conditions necessary for carrying out this work.

Physical Chemical Laboratory,
Johns Hopkins University,
May, 1906.

THE ABSORPTION SPECTRA OF CERTAIN SALTS IN NON-AQUEOUS SOLVENTS, AS AFFECTED BY THE ADDITION OF WATER.

By Harry C. Jones and Horace S. Uhler.

(EIGHTEENTH COMMUNICATION.)

[This investigation was carried out with the aid of a Grant from the Carnegie Institution.]

Apparatus.

The spectrograph, spectroscope, photographic materials, etc., used in the study of non-aqueous solutions were the same as those employed in the earlier investigation[1] of the absorption spectra of aqueous solutions. Since, however, the various parts of all the cells used for aqueous solutions were fastened together with cement, which is soluble in alcohol and acetone, it became necessary to design a cell which would not be so acted upon by the solutions to be investigated. Moreover, since no strongly adhesive cement could be found which would satisfy the requirements of being insoluble in water, alcohol, acetone, etc., it was decided to construct a cell of entirely new design, which would be absolutely free from cement of any kind.

[1] This Journal, 37, 126 (1907).

A vertical section of the cell, enlarged to twice the natural size, is shown by Plate I., and the details of the several parts may be explained as follows: In its fundamental principles, the cell consisted of 3 distinct parts: (*a*) an outer glass tube with a quartz bottom to hold the liquid; (*b*) an inner glass tube with a quartz plate at the lower end, to regulate the depth of the liquid, and to cause the upper surface of the absorbing layer of solution to be both plane and parallel to the quartz bottom of the larger glass tube; (*c*) a mechanism which would act as a stopper to the system of glass and quartz just mentioned, and which would also enable the experimenter to adjust the cell for any desired depth of absorbing layer from zero to the full capacity of the cell, *i. e.*, about 3.5 cm.

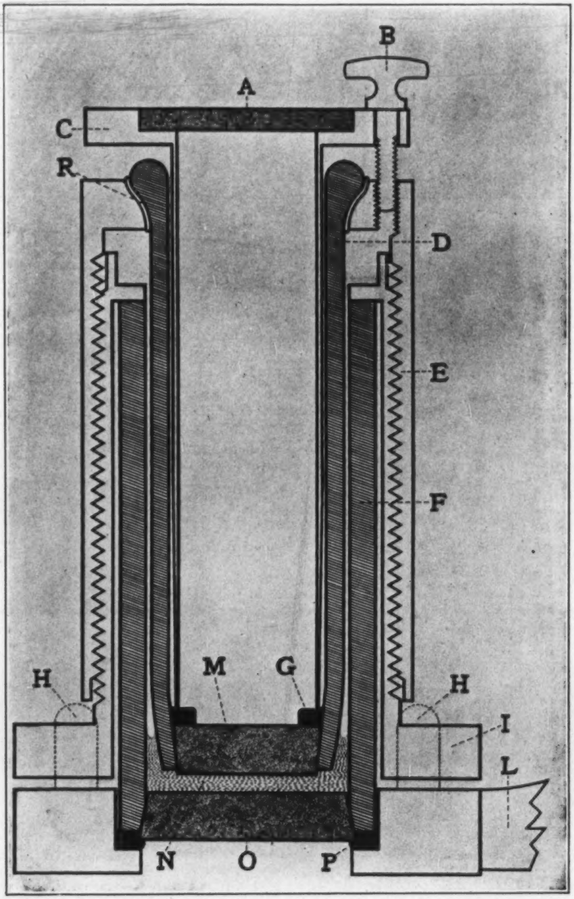
The separate parts of this piece of apparatus will be described in the order in which they would be assembled for actual use. M denotes a plane parallel plate of quartz, ground carefully in the form of a frustum of a cone, so as to fit very accurately into the conical hole at the lower end of the glass tube D. The thickness of this quartz plate was 4.6 mm., and its least diameter was 12.6 mm. The glass tube was blown with a thick shoulder at its upper end. The plate M was first slipped into place in the tube D, and then the rubber washer G was pushed down against the quartz by introducing the brass tube C into the glass tube. In order to prevent dust from entering the inner tubes, the plane parallel quartz plate A was permanently set into a cylindrical depression in the upper end of the glass tube C. This plate was 2 mm. thick and 20 mm. in diameter.

The brass tube widened out into a sort of plate at its upper end, and this projection was pierced by 3 holes at the vertices of an equilateral triangle. Through these holes suitable screws passed, and one of these is shown at B of Plate I. After the brass tube C had been introduced into the glass tube, the washer R, made of blotting paper, was slipped up over the outside of the glass tube until it would not pass through the shoulder of this tube. Then the group of parts thus far described was let down through the hole at the upper end of the hollow brass cylinder E, as far as it could go, *i. e.*, until the washer R was tightly squeezed between the glass and brass surfaces. The 3 screws were next pushed through their respective holes, and turned until the quartz plate M was forced, liquid-tight, into the conical hole in the glass tube, care being taken at the same time to so adjust the system as to have the axis of rotation of the glass tube and quartz plate parallel to the axis of the brass cylinder E. A thread of convenient pitch had been accurately cut in the inner surface of this cylinder. The purpose of this thread, as well as that of a fine line or groove which had been turned on the outside of the cylinder, in a plane at right angles to the axis of the latter, will be explained below.

Whenever the cell had been entirely taken apart, which was not often necessary, the distance between the plane of the lower surface of the quartz plate M, and the plane of the lower end of the cylinder E, had to be measured and recorded, since this distance varied with the thickness of the two washers and with the pressure exerted by the screws. The number expressing this distance was one of several numbers that had to be known in order to adjust the cell for a given depth.

The thread at E was next fitted to the thread that had been accurately cut to fit it on the outside of the brass cylinder I. Then the two cylinders were screwed together until the distance between the fine cut around the outside of E, and a certain point of the upper plane surface of the flange at the bottom of the cylinder I, had the proper value. This distance was, of course, measured along a generating line of the outer surface at E and, therefore, perpendicular to the plane just located. The assemblage of parts explained above formed a complete system in itself, and comprised all of parts L and C, using the notation of the remarks introductory to the more detailed discussion of the cell. The flange at the bottom of I was provided with 3 large and 2 small holes, and all of them pierced it parallel to the axis of the cylinder. The larger holes fitted closely over 3 pillars, H and H, while the smaller ones corresponded to 2 little

Plate I.



screws. The pillars and screws were not in the plane of the diagram. The object of the pillars and screws will be explained a little later. The cylinder I was also turned so as to have a collar on its interior near the top.

When the desired depth of absorbing liquid had been determined upon, the basis of intensity of color, etc., the distance between the line around E and the upper plane of the flange of I was found by the addition of 3 numbers. One of these was a constant of the apparatus, 1.34 cm., and the other 2 expressed, respectively, the required depth of solution, and the distance from the lower plane surface of the quartz plates M to the plane of the lower end of the brass cylinder E. As an example from practice, for a depth of 2 cm. the sum was 1.34 + 2.00 + 0.69 = 4.03 cm., *i. e.*, the 2 cylinders E and I had to be screwed around each other until the line to the flange was equal to 4.03 cm.

Conversely, knowing this distance as well as the 2 cell data, it was merely a matter of algebraic addition to obtain the effective depth of the cell.

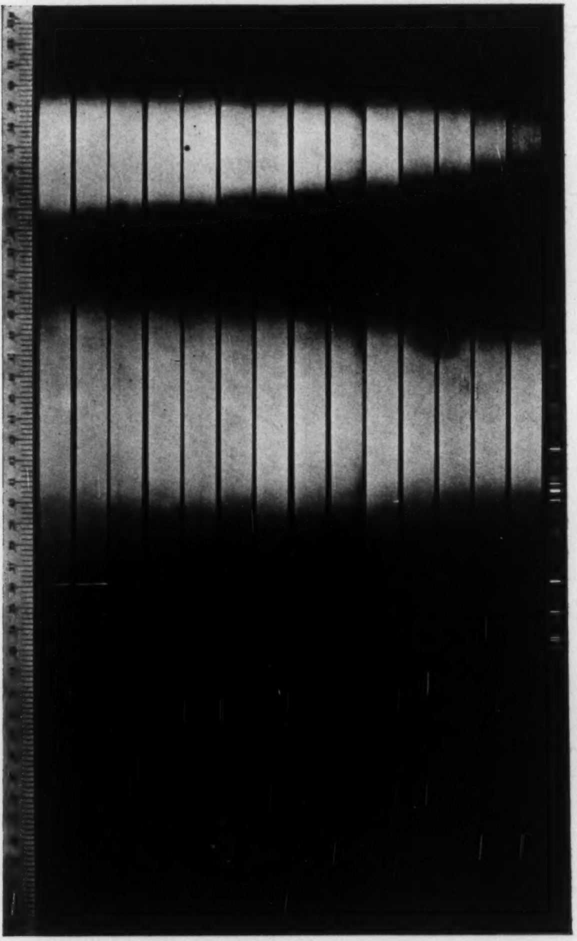
The remaining parts of the apparatus had the characteristics described below, and were assembled as follows: L denotes the handle of a stout, hollow, cylindrical plate, which formed the bottom of the complete cell. The interior of this plate was turned out so as to leave a flange at the bottom upon which the rubber washer P was placed. The 3 pillars mentioned above projected vertically from, and were rigidly attached to the plate L. Two holes had been tapped out of this plate to correspond accurately to the smooth holes of the flange of I. After laying the washer P on the flange of L, and after pushing and turning the quartz plate M tight up into the conical holes of the glass tube F, the transparent system was set vertically with its lower end resting symmetrically on the washer. The thickness and the smallest diameter of this quartz plate were, respectively, 4.6 mm. and 19 mm. The solution to be studied, N, was next poured into the vessel constituted by F and O. It was necessary to measure the depth of the liquid, and it was found convenient to make this depth 2 mm. greater than the effective depth of the cell.

The assembled system of parts A, B, C, D, G, I, M, R was next let down over the glass tube F, until the upper flange inside the cylinder I rested on top of this tube. The 3 pillars H, guided the system into the correct position, and prevented any rotation of the cylinders I and L around each other. Lastly, the 2 little screws were passed through the holes in the lower rim of I, and the 2 cylinders were screwed tightly together. This operation completed the adjustment of the cell. It is seen at once, from the preceding explanation, that the liquid or solution in question came only in contact with glass and quartz surfaces, while the vapor touched both glass and brass walls. Since the vapors of the solutions studied did not act on brass, glass and quartz, and since the apparatus did not leak, the cell gave entire satisfaction. For vapors which would attack brass, but not the silicates, it is easy to see how a system could be designed which would differ from the one just described in having coaxial glass tubes dip into a trap of some neutral liquid, instead of the brass cylinders E and I. Moreover, it would be quite possible to design the parts of the cell in such a way as to impart to the liquid the shape of a wedge or prism of adjustable angle and depth.

Solutions.

The solutions were made up as follows: A chosen volume of pure water was run out of a burette into a measuring flask. Then some of the mother solution of one of the colored salts was poured into the flask, and thoroughly mixed with the water until the volume of the resulting homogeneous solution was exactly equal to the calibrated capacity of the flask. In the following account of the work, the amount of water in a given solution will be expressed in per cent of the total volume of the solution. For example, if 5 cc. of water were made up to 200 cc. of solution, the amount of water would be given as 2.5 per cent, or simply 2.5. The colored salts used were: Cobalt chloride, copper chloride and copper bromide. The solvents employed were: Methyl alcohol, ethyl alcohol and acetone. Special precautions were taken to have both the colored salts and the solvents as free from water as possible.

Plate II.



Cobalt Chloride in Methyl Alcohol.—(See Plate II., which is reduced to seven-eighths of the original size.) The concentration of the mother solution was 0.993. The percentages of water in the solutions were 12.00, 9.50, 7.00, 6.00, 5.00, 4.00, 3.50, 3.00, 2.00, 1.50, 1.26, 1.01, 0.50, 0.000. The successive differences in per cent were 2.50, 2.50, 1.00, 1.00, 1.00, 0.50, 0.50, 1.00, 0.50, 0.24, 0.25, 0.51, 0.50. As the quantity of water increased, the color of the solution gradually changed from the purple of the mother solution to a pale pink, passing through the intermediate tints. Photographic strips, corresponding to the solutions which contained the greatest and least amount of water, are adjacent, respectively, to the numbered scale and to the comparison or spark spectrum. The depth of cell was 2.0 cm.

The spectrogram shows a region of absorption in the ultraviolet and violet, and a band in the green. The air line at 3007 A. U., was very faintly recorded by the strip corresponding to the solution which contained the greatest amount of water, but the continuous background did not extend beyond about 0.314 μ. The middle of the band in the green was 0.517 μ. As shown by the corresponding strip, transmission began near 0.373 μ, for the mother solution of cobalt chloride in the methyl alcohol. The middle of the band in the green was at 0.525 μ. Therefore, one effect of the addition of water is to shift this band towards the blue. It is interesting to note, in this connection, that the center of the absorption band in the green was displaced towards the red by about 100 A. U., when the solvent was changed from water alone[1] to methyl alcohol. This absorption band widened very gradually as the amount of water in the successive solutions decreased. In fact, for the mother solution the negative strip indicated that transmission began near 0.505 μ and 0.540 μ at the sides of this absorption band. The band was very weak for the solution which contained the greatest amount of water. It must, however, be remembered that the other solution was not quite 0.1 N, cobalt chloride being only slightly soluble in methyl alcohol.

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[1] THIS JOURNAL, 37, 162 (1907).

Eye observations of typical solutions of the set gave the following results: The depth of cell used was 3.0 cm. The mother solution had a clear purple color, with a decided reddish tinge, when viewed by diffuse daylight transmitted through the cell. Transmission began about 0.766 μ, and extended to the beginning of the absorption band in the green. Weak, partial absorption appeared in the red at 0.704 μ. The brightest region of transmission was in the immediate neighborhood of 0.625 μ, *i. e.*, in the yellow. No narrow absorption bands in the red, orange or yellow, such as were observed for aqueous solutions of cobalt chloride, were visible. The band in the green was narrow but intense, its maximum being near 0.540 μ. It was much more abrupt on the less than on the more refrangible side. For one definite exposure, a photographic film does not necessarily show the position of the maximum of intensity of an asymmetric absorption band, so that it is not surprising to find 0.525 μ for the center of the photographic band, and 0.540 μ, for the maximum of absorption with the prism spectroscope. To see if there are any other absorption bands, the cell was filled to the brim of the larger glass tube, and the rest of the system was not put in place. In this manner a column of solution 4.5 cm. long was obtained. The several faint maxima and minima of transmission could be seen in the red. If the solution could have been made more concentrated, or better, if the cell had been deeper, it is extremely probable that all the bands observed in aqueous solutions could have been seen with the alcoholic solution in question. As the spectra of the solutions which contained greater and greater amounts of water were brought into the field of view, it was observed that the various regions of absorption grew weaker and weaker, and that the entire spectra remained qualitatively similar to the spectrum of the mother solution. Of course, the regions of weak absorption around 0.704 μ soon disappeared. The maximum of intensity of the absorption band in the green had the wave length 0.525 μ, for the solution which contained the greatest percentage of water, (12.00). Consequently, the maximum of this band was displaced about 150 A. U. towards the blue, when

Plate III.

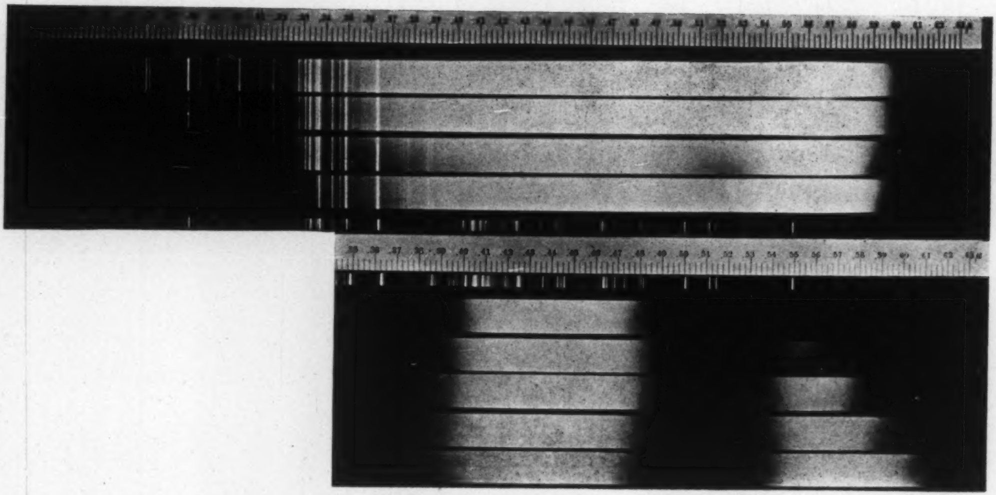
the amount of water in the solution was changed from 0.000 to 12.00.

Cobalt Chloride and Ethyl Alcohol. — (See Plates III and IV(*b*).) The concentration of the mother solution of cobalt chloride in ethyl alcohol was 0.0967. The percentages of water in the solution were 20.0, 10.0, 8.0, 7.5, 7.0, 6.0, 5.5, 5.0, 4.0, 3.0, 2.0 and 0.0. The successive differences in per cent were 10.0, 2.0 0.5, 0.5, 1.0, 0.5, 0.5, 1.0, 1.0, 1.0, 2.0. As the quantity of water decreased, the colors of the solutions changed from pink, through various shades of violet, to deep blue. The photographic strips corresponding to the solutions which contained the greatest and least amounts of water, are contiguous, respectively, to the numbered scale and to the comparison spectrum of Plate III. This spectrogram will be discussed before Plate IV(*b*). The depth of the cell was 2.00 cm; but as this number is given from memory, it may not be exact. As would be expected, the same general regions and bands of absorption were possessed by the solutions of cobalt chloride in ethyl alcohol and water, as by those in which methyl alcohol took the place of ethyl alcohol. The negative strip pertaining to the solution which contained the greatest amount of water, barely recorded the intense zinc line of wave length 2502.1 A. U. The continuous background ceased about 0.280 μ. The middle of the band in the green as shown by the negative was near 0.516 μ. For the solution whose percentage of water was 2.0, the negative strip gave 0.519 μ as the middle of the band in the green. Hence, the photographic band was displaced towards the blue by about 30 A. U., as the percentage of water was increased from 2.0 to 20.0. The strip corresponding to the mother solution showed transmission between the extreme limits 0.384 μ and 0.508 μ. The last 3 strips, and especially the very last one, showed the existence of appreciable general absorption in the yellow and orange. The negative for Plate IV(*b*) was taken with a Cramer trichromatic plate. The solutions used were the last 5 of the set of 12, in other words, the 5 which contained the smallest amounts of water. The strip pertaining to the mother solution is closest to the scale. The depth of the cell was 2.00 cm. The exposure for the Nernst filament lasted for 2 minutes. The negative recorded the middle of the absorption band in the green as at 0.510 μ, for the solution which contained 5.00 per cent of water. The 5 strips show distinctly the gradual shift of the middle of this band towards the red, as the quantity of water in the solutions decreased from 5.00 to 0.00 per cent. They also exhibit the progress of absorption both in the violet and in the orange and yellow. In fact, the strip pertaining to the mother solution shows no transmission of the yellow. The middle of the region of transmission between the band in the violet and the band in the green, moved towards the red, whereas the center of the bright region between the band in the green and the band in the orange shifted towards the blue, as the percentage of water decreased.

The results obtained by eye observations with the Hilger spectroscope were as follows: The depth of cell used was 2 cm. With only air in the path of the beam of light, the spectrum began near 0.776 μ. The mother solution transmitted faintly a band of red from 0.775 μ to 0.735 μ. The more refrangible limit was quite well defined. An intense region of absorption extended from 0.735 μ to 0.575 μ. Transmission began again in the blue-green. This color, however, was weak. Absolutely no light of shorter wave length than 0.417 μ could be seen, which shows that the ultra-violet region of absorption extended into the visible spectrum by at least 170 A. U.

The solution which contained 2 per cent of water transmitted a band of red, like the mother solution. Then the absorption was complete as far as 0.629 μ. Faint transmission began at 0.269 μ and passed over into rather strong transmission in the vicinity of 0.597 μ. In other words, a single broad band possessed by the mother solution had broken up into 2 bands, of which the more refrangible was much less intense and well defined than its companion in the red. A relatively weak spot in the transmission appeared near 0.52 μ.

The solution which contained 3 per cent of water had a complicated spectrum, very much like the spectra belonging to aqueous solutions of cobalt chloride to which a comparatively large quantity of calcium chloride, of calcium bromide,



Plates IV(a) and IV(b).

or of aluminium bromide had been added. The maximum of transmission in the red was near 0.734 μ, and the adjoining region of intense absorption had its maximum at about 0.690 μ. Then a series of bands of incomplete opacity and transparency succeeded one another. The position of the maxima of absorption were recorded as 0.636 μ, 0.615 μ, 0.600 μ, with the brightest transmission at 0.627 μ; 0.608 μ marked the center of a very faint maximum of transmission. The next region of relatively strong transmission extended from 0.596 μ to about 0.535 μ. The band in the general neighborhood of 0.52 μ was weak and very diffuse at its limits.

For the solution containing 4 per cent of water there were maxima of transmission at 0.730 μ and 0.627 μ. The maxima of the absorption band had the wave lengths 0.695 μ, 0.636 μ, 0.615 μ and 0.600 μ. The stronger band at 0.695 μ transmitted a little light even at its maximum. The bands at 0.615 μ and 0.600 μ were very faint. The band in the green was too diffuse and indefinite to have the position of its center or even of its maximum determined. For the 5.5 per cent solution the bands at 0.636 μ, 0.615 μ, 0.600 μ had become so extremely faint that they could only be seen by moving the spectrum across the field of view of the telescope. All the remaining bands were much weaker.

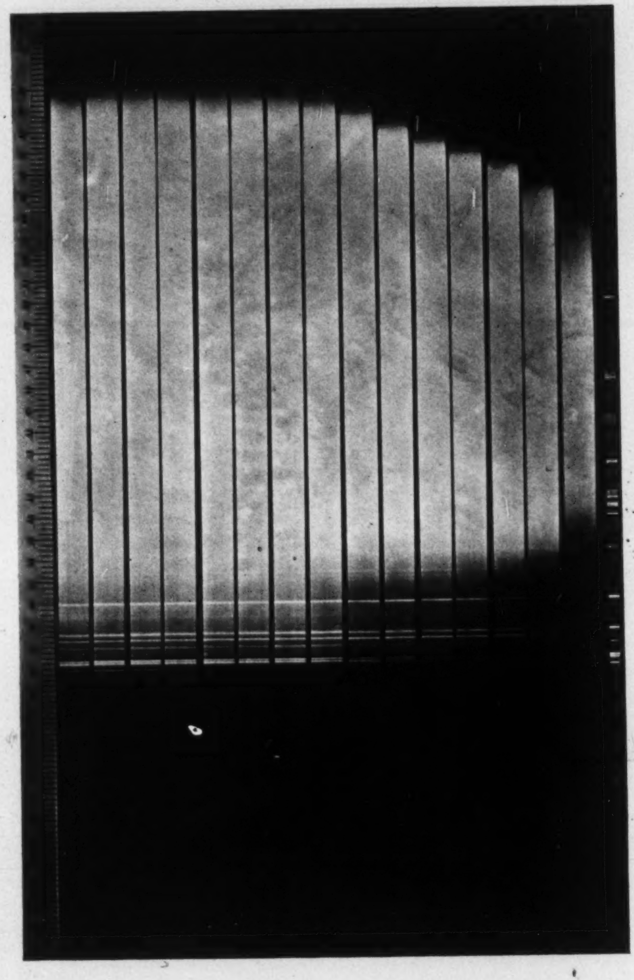
For the 7 per cent solution the band in the red had become very weak, while for the 8 per cent solution it had become a mere shadow and lost its identity as a band.

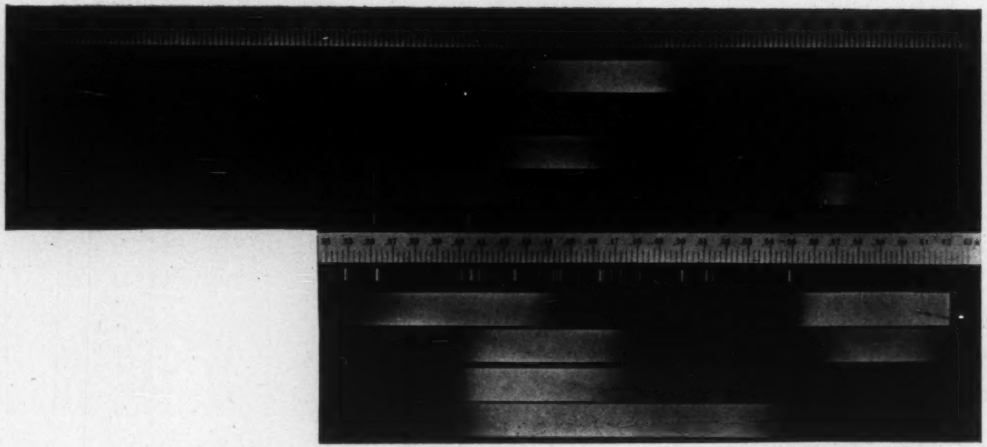
A solution which contained 40 per cent of water exerted very slight absorption in the extreme red, and very weak diffuse absorption in the blue-green.

Cobalt Chloride in Acetone.—(See Plate V., which is reduced to seven-eighths of its original size.) The concentration of the mother solution of cobalt chloride in acetone was 0.0154. The percentages of water in the solutions were 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2, and 0. Each successive difference in this sequence equals 2. When placed in the cell, at a depth of 2 cm., the solutions whose percentages of water varied from 28 to 16, inclusive of the latter number, were delicate pink. Beginning with the solutions having 14 per cent of water, the color changed to blue, which was at first very faint and then gradually increased as the amount of water decreased. The mother solution had a very deep blue color. The photograph strips adjacent to the numbered scale and to the comparison spectrum correspond, respectively, to the solutions that contained the greatest amount of water and no water at all. The spectrogram shows the existence of a region of very intense absorption in the ultra-violet, and another region in the orange. No band appeared photographically in the green. The negative strip for the 28 per cent solution showed that the ultra-violet region of absorption ended abruptly at 3250. That this limit of absorption did not vary rapidly as the amount of water decreased, is shown by the fact that the strip for the 2 per cent solution gave the wave length of complete absorption as 3329. In other words, this limit only moved by about 80 A. U., while the percentage of water changed from 28 to 2. In addition to the abrupt limit of absorption, the existence of ever increasing weak absorption of the extreme violet and least refrangible ultra-violet, is shown by the last 5 or 6 strips, which correspond to the solutions that contained smaller amounts of water. For the mother solution this general absorption was relatively strong. Although the strip for the mother solution recorded very faintly the air line at 3331.5, nevertheless, the continuous background only began to grow strong near, say, 0.375 μ. The last 8 or 9 negative strips showed distinctly the existence of absorption in the orange and yellow. Also the more refrangible limit of this band did not shift in direct proportion to the percentage of water in the successive solutions. The strip for the mother solutions shows that transmission of sufficient intensity to affect the photographic film stopped at about 0.554 μ.

The spectroscopic study of the bands in the red and orange brought out the following facts: The cell depth was 2.00 cm. For the mother solution transmission began near 0.570 μ and increased to about 0.554 μ. The green and blue regions are not very bright, and the nearest approach to transparency seemed to be in the indigo. Visible transmission ceased at

Plate V.





Plates VI(a) and VI(b).

Plate VII.

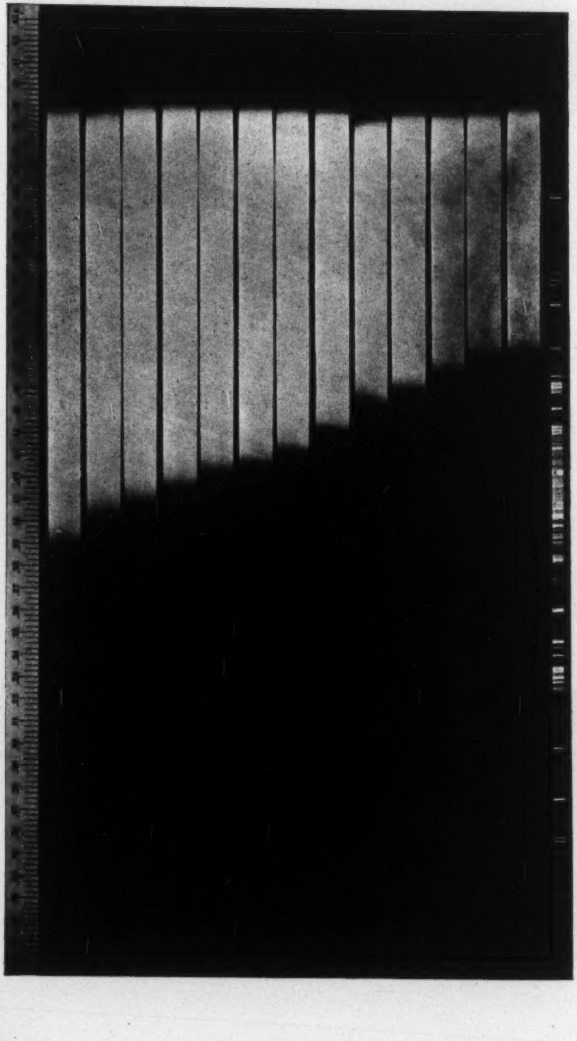


Plate VIII.

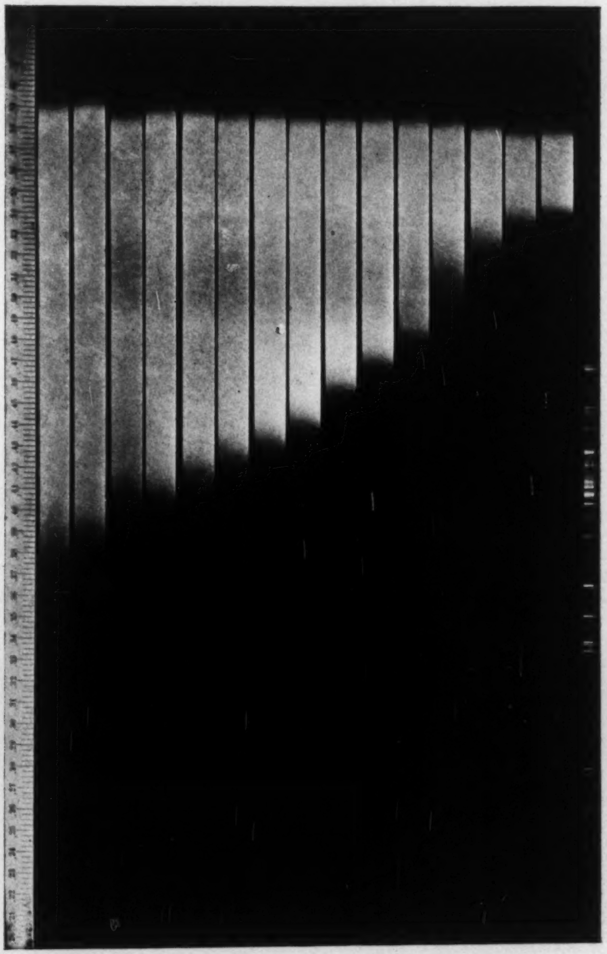
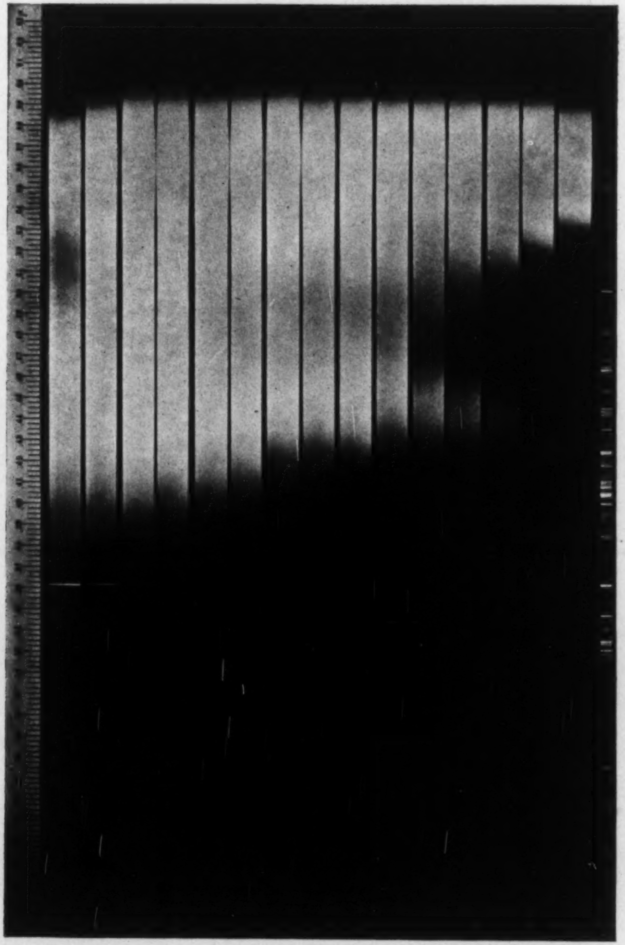
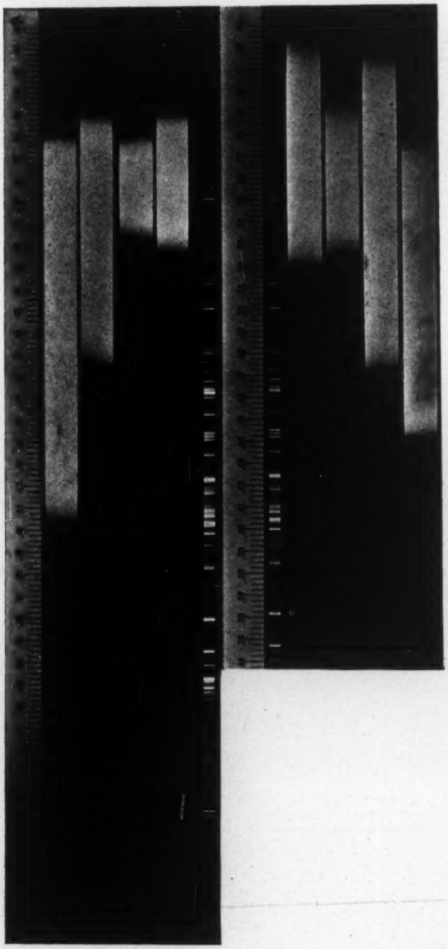


Plate IX.





Plates X(a) and X(b).

Plate XI.

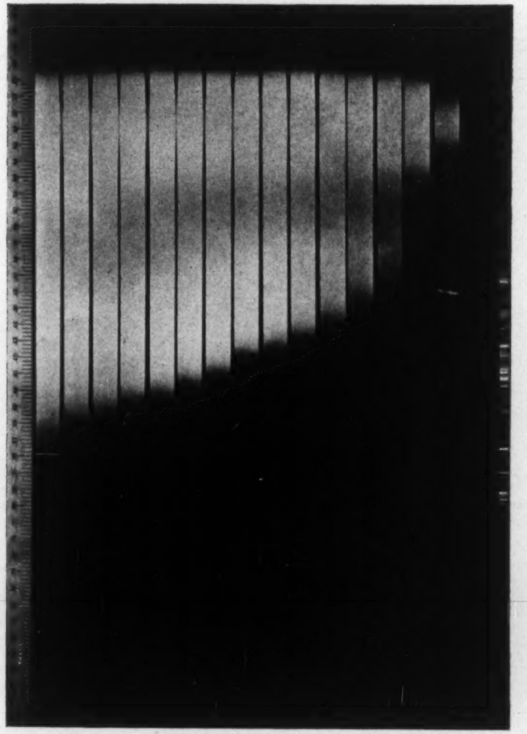


Plate XII(a). Plate XII(b).

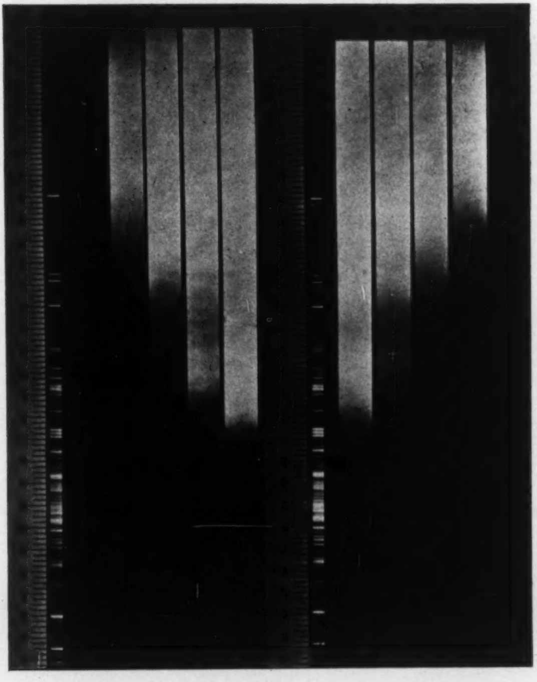
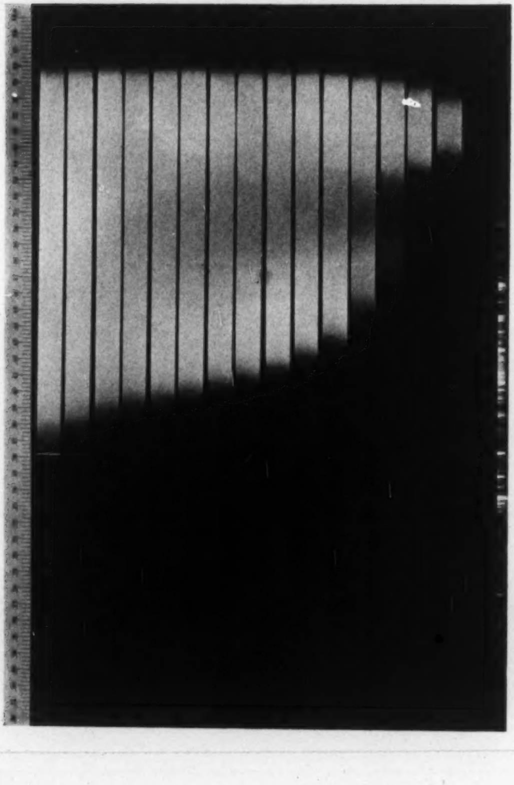
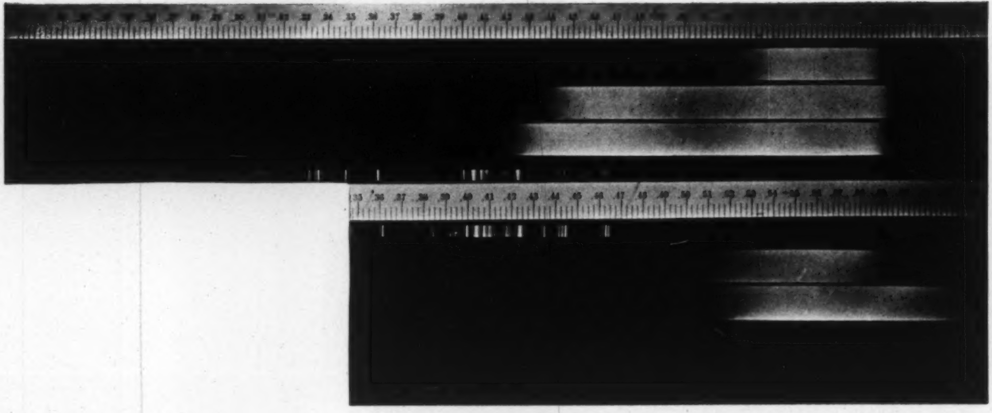


Plate XIII.





Plates XIV(a) and XIV(b).

0.424. The spectrum of the 4 per cent solution was qualitatively like that of the mother solution. The wave lengths which corresponded to 0.570 μ, 0.554 μ and 0.424 μ for the mother solution were, respectively, 0.599 μ, 0.574 μ and 0.416 μ, in the case of the 4 per cent solution. The solution which contained 6 per cent of water was the first to show definite absorption bands. It transmitted very faintly the red from 0.77 μ to 0.731 μ. One absorption band extended from 0.731 μ to 0.630 μ, and another from 0.616 μ to about 0.596 μ. Slight transmission separated these 2 bands of complete absorption. The complete spectrum for the 8 per cent solution was more complicated than that of the 6 per cent solution. The red was faintly transmitted from 0.77 μ to 0.721 μ, with the maximum of brightness near 0.741 μ. Complete absorption from 0.721 μ to 0.651 μ was followed by very weak transmission between 0.651 μ and 0.634 μ. A strip of relatively weak transmission which, however, was much more intense than its less refrangible neighbor, began at 0.634 μ and had its middle at 6255 A. U. This was followed by 2 comparatively narrow, symmetrical bands of almost complete absorption, whose maxima had the wave lengths 0.613 μ and 0.6005 μ. The middle of the intervening and very faint band of transmission was at 0.607 μ. The spectrum for the 10 per cent solution was very much like that of the 8 per cent, the absorption bands, of course, being somewhat weaker. For the 12 per cent solutions the bands were very faint indeed. The strongest band had the approximate wave length 0.700 μ. The narrow bands at 0.613 μ and 0.6005 μ, could only be seen by moving the spectrum across the field of view. The 14 per cent solution showed only one absorption band. This band was in the extreme red and was very weak. The 16 per cent solution had no visible bands, as such. The transmission from the bluish color of 14 per cent, to the pinkish tinge of the 16 per cent solution, was due to the gradual disappearance of the absorption bands in the red, and not to an abrupt or continuous change of any kind whatsoever. The solutions having more than 16 per cent of water showed no absorption bands in the spectroscope.

Before taking up the discussion of the copper salts, it is desirable to compare the spectra of the mother solutions of cobalt chloride with one another, and to consider how much of the ultra-violet absorption was due to the solvents themselves. See Plates VI(*a*) and VI(*b*). Consider first the negative for VI(*a*). The concentrations of the cobalt chloride in acetone, in ethyl alcohol, in methyl alcohol and water, were, respectively, 0.010, 0.097, 0.099 and 0.325; this last solution, diluted from the original mother solution, was used in the preceding study of aqueous solutions. The first solution, which was not the mother solution for Plate V., was blue, with a slight greenish tinge. The second solution was blue with a slight reddish tinge. The second solution was deeper blue than the first, due largely to the difference in concentration. The third and fourth solutions were, respectively, purple and red. The photographic strips nearest to the numbered scale and to the comparison spectrum correspond, respectively, to the solutions in acetone and in water. The 4 strips are in the same order as that in which the solutions are named above. The depth of the cell was 2.048 cm. The strip pertaining to the acetone solution recorded very faintly the intense doublet at 3330, but the extreme limits of the continuous background were 0.370 μ and 0.550 μ. The strip corresponding to the ethyl alcohol solution gave the extreme limits of transmission as 0.388 μ and 0.496 μ. The negative strip pertaining to the methyl alcohol solution gave the limits of one region of transmission as 0.385 μ and 0.495 μ. Faint transmission was recorded from 0.555 μ, towards the red. An absorption band extending from 0.495 μ to 0.555 μ. The density of the negative was greater in the region of the blue and violet for the solution in methyl alcohol than for the one in ethyl alcohol. Also the maxima of transmission as given by the negative for the solutions in acetone and in methyl alcohol were, respectively, near 0.470 μ and 0.442 μ. The strip for the aqueous solution showed the trace of a line at 2502.1, but the continuous background faded away near 0.288 μ. The band of absorption in the green comprised the region from 0.452 μ to 0.551 μ.

The contrasts of the regions of absorption and of transmission of the 4 solutions under consideration, are very distinctly shown by Plate VI(*b*). The negative for this spectrogram was taken with a Cramer trichromatic plate. The solutions were the same as for Plate VI(*a*), and their spectra were photographed in the same order. The strip corresponding to the aqueous solution is adjacent to the scales. The depth of the cell was 2 cm., and the length of exposure for the glower was 2 minutes. The extreme limits of transmission for the solution of acetone were 0.370 μ and 0.562 μ. The corresponding limits for the solutions in methyl alcohol were about 0.385 μ and 0.497 μ. The strips pertaining to the last 2 solutions showed no return to transparency in the yellow and orange. The solution in methyl alcohol transmitted light from about 0.390 μ to 0.500 μ. This was followed by an absorption band from 0.500 μ to 0.547 μ. The aqueous solution had a band of complete absorption from about 0.462 μ to 0.543 μ. The region of transmission in the yellow and yellow-orange, was much more intense for the aqueous solution than for the one in methyl alcohol. The shifts experienced by the centers of the regions of absorption and transmission, when the solvents were changed, due allowance being made for the several concentrations, were large, and are rather strikingly shown by Plate VI(*b*). The results of eye observations on the spectra of the 4 solutions in question, have already been given, so that nothing more than a brief résumé of the facts is necessary. The solution in acetone transmitted a faint band of red, the middle of which was near 0.761 μ. The solution in methyl alcohol transmitted more strongly a region of red from about 0.775 μ to 0.735 μ. The spectrogram of Plate VI(*b*) gives the photographic positions of the less refrangible limit of the absorption band in the green. The solution in methyl alcohol showed a weak absorption band near 0.704 μ, while the aqueous solution was too dilute to give the bands in the red. Therefore, that region of absorption which may be called, for brevity, the band in the green, moved its center to shorter and shorter wave lengths, as the solvents successively used were acetone, ethyl alcohol, methyl alcohol and water.

Plate IV(*a*) gives the ultra-violet absorption of the 4 solvents used. The strip adjacent to the numbered scale corresponds to distilled water, and the next strip belongs to methyl alcohol. The strip nearest to the comparison spectrum corresponds to acetone. The remaining strip resulted from light transmitted by ethyl alcohol. The depth of the cell was 1.41 cm. As is well known, water is exceptionally transparent to short light waves, so that the negative strip for this liquid recorded as many lines in the remote ultra-violet as was shown by the comparison spectrum. The shortest wave length given by the strip for methyl alcohol was 2313.0. The strong cadmium line, however, was just barely visible on the negative. The intense lines at 2558.0, 2573.1 and 2712.6 were rather fully transmitted. The continuous background for waves more refrangible than 2748.7 was extremely weak. The third strip showed that ethyl alcohol was more transparent than methyl alcohol to the remote ultra-violet, since it recorded distinctly the lines at 2265.1, 2288.1, 2313.0 and 2321.2. On the other hand, the lines at 2558.0, 2573.1 and 2721.6 were not quite as strong after passing through the ethyl alcohol as they were after emerging from the methyl alcohol. Taking the continuous background into account, as well as the spark lines, the negative shows that methyl alcohol has a one-sided region of absorption in the ultra-violet, whereas ethyl alcohol has a region of semitransparency in the neighborhood of 0.230 μ, with strong absorption on both sides. For all ultra-violet and visible waves less refrangible than 2748.7 the transmission of these 2 alcohols seems to be identical. Acetone showed intense selective absorption in the ultra-violet, because the associated photographic strip recorded nothing beyond 3282.4. This line was very much weakened, and the correct limit of this region of absorption was 3302.7. The conclusion is that the ultra-violet absorption of the cobalt chloride was only masked by that of the solvent in the case of acetone. In all of the other examples studied, the ultra-violet absorption was due largely to the cobalt chloride in the solution, and not so much to the solvents as such.

Copper Chloride in Methyl Alcohol.—(See Plate VII.) The concentration of the mother solution of copper chloride was 0.283. The percentages of water in the solutions of the series were: 40, 36, 32, 28, 26, 24, 22, 20, 16, 12, 8, 4, and 0. All the successive differences in this sequence of numbers were equal to 4 per cent, except the fourth, fifth, sixth and seventh. Each of the 4 exceptional increments was equal to 2 per cent. To obtain a general idea of the dependence upon the amount of water present of the limit of absorption of the band, which included the ultra-violet, it is convenient to omit the fifth and seventh photographic strips from consideration. As the amount of water decreased, the color of the solutions varied from greenish-blue, through pure green, to a green with a yellow tint.

The strip corresponding to the 40 per cent solution is adjacent to the numbered scale, and that belonging to the mother solution lies next to the comparison spectrum. The depth of the cell was 2.40 cm. The negative showed only 1 region of absorption, and it included the entire ultra-violet, the negative strips corresponding, respectively, to the solution which contained the greatest amount of water, and to the one which was anhydrous, gave the very beginnings of transmission as 0.375 μ and 0.480 μ. The complete spectrogram shows that the increments of absorption decreased gradually as the percentage of water decreased in arithmetical progression.

The spectroscope revealed the existence of a one-sided region of absorption in the red. The depth of cell used was 2 cm. The limit of visible transmission moved towards the infra-red, as the quantity of water in the solutions increased. The approximate wave lengths of this limit were 0.65 μ and 0.67 μ, respectively, for the mother solution and for the solution which contained 40 per cent of water.

Copper Chloride in Ethyl Alcohol.—(See Plate VIII., which is reduced to seven-eighths of the original size.) The concentration of the mother solution of copper chloride was 0.321. The percentages of water in the solutions of the complete set were 56, 52, 48, 44, 40, 36, 32, 28, 24, 20, 16, 12, 8, 4 and

0. Each successive difference equals 4 per cent. The colors of the liquids, when viewed in the cell, varied from blue, through greenish blue, bluish green, green, and yellowish green to olive, as the percentage of water decreased from 56 to 0. The photographic strip contiguous to the numbered scale belongs to the solution which contained 56 per cent of water. The next strip corresponds to the 52 per cent solution, etc., until, finally, the strip adjacent to the comparison spectrum corresponds to the anhydrous mother solution. The depth of the cell was 2 cm. The spectrogram shows a one-sided region of strong absorption in the ultra-violet and violet, and suggests another like region in the yellow and orange. The negative strip corresponding to the solution which contained the greatest amount of water, recorded faintly the strong cadmium doublet at 3467, but the continuous background faded out at near 0.350 μ. Transmission began weakly at 0.520 μ for the mother solution. The curve outlined by the ends of the photographic strips, appeared to be convex toward the ultra-violet region of absorption, throughout the greater part of its course; whereas, in general, the curves obtained for copper chloride, whether in water alone or in water which also contains some dehydrating agent, were concave towards the left.

The spectroscope showed that there was an absorption band in the infra-red, which extended into the visible spectrum. For the anhydrous mother solution transmission began at about 0.635 μ, and for the solution which contained the greatest amount of water, it commenced at 0.700 μ. Eye observations on the spectra of the solutions in question showed that the limit of absorption in the red receded to longer wave lengths as the percentage of water in the solution increased.

Copper Chloride in Acetone.—(See Plate IX. which is reduced to seven-eighths of the original size.) The concentration of the mother solution of copper chloride in acetone was 0.022. The percentages of water in the various solutions of the set were 28, 24, 22, 20, 18, 16, 12, 10, 8, 6, 4, 3, 2, 1 and 0. The first and sixth differences were 4 per cent. The last 4 increments reached 1 per cent, and all the remaining increments

2 per cent. The solutions varied in color from bluish green to dark olive, as the percentage of water decreased from 28 to 0. The strip most remote from the numbered scale corresponds to the anhydrous mother solutions, the next strip pertaining to the solution which contained 11 per cent of water, etc., until the strip adjacent to the scale corresponds to the solution which contained the greatest amount of water. The depth of the cell was 2 cm. The complete spectrogram shows a region of strong absorption in the ultra-violet and violet, and also a band in the blue-green. The negative strip pertaining to the solution which contained 28 per cent of water recorded faintly the zinc doublet at 3345, but the continuous background practically ceased at 0.344 μ. The locus of the limits of the region of absorption, which comprises the entire ultra-violet, is a smooth curve concave towards this region. The strip corresponding to the 4 per cent solution barely indicated the existence of an absorption band whose center was at 0.473 μ. The remaining strips, which correspond to the solutions that contain less than 4 per cent of water, show that the band both widened out rapidly, and had its center displaced slightly towards the red, as the amount of water decreased. In fact, a strip pertaining to the anhydrous solution showed that the band in the blue-green had united with the wide region of absorption in the ultra-violet, so that no light of wave length shorter than 527 μ was transmitted. The middle of the transparent region between the two bands of absorption in question was at about 0.436 μ.

Eye observations with the spectroscope, and with the cell 2 cm. deep, brought out the following facts: The mother solution transmitted, freely, orange, yellow and yellow-green. Its spectrum began at 0.706 μ and ended near 0.507 μ. Because the spectrum began at 0.775 μ, when the cell was not in the path of the light incident upon the slit of the spectroscope, it is evident that the mother solution absorbed all the deep red. The 2 per cent solution began to transmit at 0.727 μ. The transmission spectrum began to be much weakened near 0.503 μ, and showed a weak band of partial absorption at the more refrangible side of the wave length. Faint light could be distinguished as far as 0.435 μ. The minimum of transmission in the blue-green could also be observed in the case of the 4 per cent solution. The solution which contained the greatest amount of water began to transmit at about 0.750 μ. The entire series of observations showed that the more refrangible limit of the band which absorbed the red, receded towards the infra-red as the percentage of water in the solution increased.

For the sake of comparison, the spectra of the solutions of copper chloride in the 4 pure solvents were recorded side by side, photographically. See Plates X(*a*) and X(*b*). The concentrations of the solutions in water, in methyl alcohol, in ethyl alcohol and acetone as solvents were, respectively, 0.795, 0.283, 0.321, 0.022. The depth of cell used was 1.50 cm. for both plates. In the cell the aqueous solution was blue, the solution in methyl alcohol was yellowish green, the solution in ethyl alcohol was very dark green and the solution in acetone was brownish yellow. The negative strips corresponding, respectively, to the solutions in water and in acetone, are adjacent to the numbered scale and to the comparison spectrum. The strip nearest to the one that pertains to the aqueous solution, corresponds to the solution in methyl alcohol. The negative of Plate X(*a*) showed that the extreme limits of transmission for the aqueous solution were 0.397 μ and 0.598 μ. Only the more refrangible limit of the region of visible transmission could be recorded by the Seed film, for the solution in methyl alcohol. This limit was given as 0.472 μ. The limits of faint transmission for the solution in ethyl alcohol, were recorded as 0.523 μ and 0.598 μ. The negative strip corresponding to the solution in acetone as solvent, showed that transmission began at about 0.519 μ, and extended beyond the region of sensibility of the photographic emulsion.

The negative for Plate X(*b*) was taken with a Cramer trichromatic plate. The concentrations of the non-aqueous solutions were the same as for Plate X(*a*). The concentration of the aqueous solution of copper chloride was 1.590, *i. e.*, twice as great as formerly. The solution was green with a bluish tinge. The length of the exposure for the Nernst glower was 2 minutes. The photographic strips succeed one another in exactly the same order for Plate XI(*b*) and for Plate XI(*a*). However, the strip corresponding to the solution in acetone is adjacent to both scales, while the one pertaining to the aqueous solution is nearest to Plate X(*a*). The extreme limits of transmission were shown by the negative to be 0.431 μ and 0.591 μ for the aqueous solution. The strip corresponding to the solution in methyl alcohol showed that transmission began near 0.462 μ, and only became weakened to a very slight extent at the extreme end of the plate. The strip pertaining to the solution in ethyl alcohol gave the limits of transmission as 0.512 μ and 0.618 μ. The acetone solution began to transmit at about 0.507 μ, and continued to do so beyond the field of view of the spectrograph. The results of eye observations, combined with the data obtained photographically, show that as the solvent for copper chloride was successively water, ethyl alcohol, methyl alcohol and acetone, the middle of the region of transmission in the visible spectrum moved to longer and longer wave lengths.

Copper Bromide in Methyl Alcohol. — (See Plates XI., which is reduced to three-fourths of the original size, and XII(*a*).) The concentration of the mother solution of copper bromide in methyl alcohol was 0.122. Instead of being made up in the usual way, the solutions were prepared by measuring the volume of the mother solution, and then adding water to the mark on the measuring flask, the percentages of water in the solutions of the series being 52, 44, 40, 36, 32, 28, 24, 20, 18, 16, 14, 12, 10, 8, 4 and 0. Therefore, the successive differences in percentage were 8, 4, 4, 4, 4, 4, 4, 2, 2, 2, 2, 2, 2, 4, and 4. In the cell, which was at a depth of 0.76 cm., the first 4 solutions were practically colorless, the next 3 were of an extremely pale, greenish yellow color, the succeeding 6 were greenish yellow, the third from the last was brownish yellow and the last 2 were dull brown. For the spectrogram of Plate XI. the strips corresponding, respectively, to the solution which contained the greatest amount of water, and to the anhydrous solution, are adjacent to the numbered scale and to the comparison spectrum. The negative strip corresponding to the 52 per cent solution, recorded faintly the zinc line at 3262.4, but the continuous background hardly extended as far as 0.334 μ. The strip pertaining to the 8 per cent solution, showed that weak general absorption had set in beyond the limit of the intense ultra-violet region of absorption. In other words, transmission began at about 0.453 μ, and continued to be relatively weak as far as 0.527 μ. Of course, the maxima and minima of photographic sensibility exaggerated the phenomenon in question. The strip corresponding to the 4 per cent solution showed very faint transmission from 0.482 μ to about 0.530 μ.

The strip pertaining to the mother solution recorded extremely faint transmission from 0.543 μ towards the red. The last 3 strips showed the existence of general absorption in the orange. Due allowance being made for the values of successive differences in the amounts of water in the solutions, as well as for variations in photographic sensibility, the complete spectrogram shows that the curve for the limit of ultra-violet absorption was convex towards the region of shortest waves, at least throughout the greater part of its course. The negative for Plate XII(*a*) was taken with a Cramer trichromatic plate. It gave the spectra of the 5 solutions of the set in question, which contained the smallest percentages of water, including no water at all. The cell depth was, as above, 0.76 cm. Each exposure to the light from the glower was 2 minutes. The negative strip, corresponding to the 8 per cent solution, showed that transmission began at about 0.453 μ, and remained relatively weak as far as 0.503 μ. The strip pertaining to the solution which contained 4 per cent of water, gave 0.498 μ as the wave length of the very beginning of faint transmission. The strip belonging to the anhydrous mother solution showed an extremely faint transmission from about 0.530 μ to the end of the spectrogram.

Eye observations with the spectroscope confirmed qualitatively the above results, and also brought out some additional facts relative to the red region in the spectrum. For the mother solution transmission began at 0.715 μ, rose to maximum near 0.651 μ, and then decreased to a very small value in the neighborhood of 0.593 μ. Transmission was extremely weak from 0.593 μ to 0.520 μ, *i. e.*, to the beginning of the ultra-violet region of complete absorption. There appeared to be a slight minimum of transmission at 0.575 μ, and a weak maximum at 0.540 μ. Red and orange were, obviously, the only colors appreciably transmitted. The spectrum of the 4 per cent solution was very much like that of the anhydrous solution. The spectra of both solutions agree in having a relatively bright region of transmission in the red, followed by a long, comparatively weak region in the direction of the shorter wave length. The maximum of transmission was near 0.640 μ, and complete extinction commenced at about 0.490 μ. Green and blue were transmitted much more strongly by the 4 per cent solution than by the mother solution. The spectrum of the 8 per cent solution showed that the region of weak transmission had left the green and comprised only the blue. There were no appreciable contrasts in the transmitted regions of the spectra of the remaining solutions in the series. As the percentage of water increased from 0 to 52, the end of the absorption band in the red receded gradually from about 0.715 μ to 0.755 μ.

Copper Bromide in Ethyl Alcohol.—(See Plates XII(*b*) and XIII., which latter is reduced to three-fourths of the original size.) The concentration of the anhydrous mother solution was 0.101. The percentages of water in the series were 36, 32, 28, 26, 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4 and 0. Therefore, all the successive differences were equal to 2 per cent except the first 2 and the last 1, and each of these is equal to 4 per cent. Viewed in their bottles, the solutions varied in color from bluish green, through the various shades of green and olive, to very dark brown, as the amount of water decreased from 36 to 0 per cent. The mother solution was sensibly opaque except in very thin layers. The same succession of colors was shown by the solutions when in the the cell at a depth of 0.24 cm., with the exception that the first 4 or 5 solutions appeared practically colorless.

The photographic strips which correspond, respectively, to the solution that contained the greatest amount of water, and to the one that was anhydrous, are adjacent to the numbered scale and to the comparison spectrum of Plate XII. The cell depth for both plates, XII. and XIII., was 0.24 cm. The negative strip belonging to the 36 per cent solution recorded the faintest trace of the cadmium line at 3261.2, but the continuous background became very weak near 0.340 μ. The spectrogram, taken as a whole, shows that the locus of the limit of absorption of the region which included the ultra-violet, was a smooth curve, convex towards the region of shortest wave length. Also the last 6 or 7 photographic strips, show that there was general absorption in the orange and red. The strips corresponding to the solution whose percentages of water were 10, 8, 6, and 4, showed that a region of weak general absorption formed a continuation into the blue and green, of the region of intense absorption of the ultraviolet and violet. The strength of this general absorption increased rapidly as the amount of water in the solutions decreased. This is exactly the same phenomenon as was exhibited by the negatives for the solutions of copper bromide in methyl alcohol and varying amounts of water. The strip corresponding to the anhydrous solution recorded extremely faint transmission from 0.544 μ towards the red.

The negative for Plate XII was taken with a Cramer trichromatic plate. The spectra photographed corresponded to the 5 solutions of the series containing the smallest amounts of water, which included, of course, no water. The depth of the cell was 0.24 cm. The exposures to the light from the Nernst filament were each 2 minutes. The strip nearest to the scales corresponds to the solution which contained 10 per cent of water. The fifth strip, counting away from the scales, pertains to the mother solution. The negative strip corresponding to the 6 per cent solution, recorded the beginning of very faint transmission near 0.451 μ, and showed that relatively intense transmission did not commence until about 0.510 μ. The wave lengths corresponding, respectively, to the beginning of faint and strong transmission, were given as 0.493 μ and 0.533 μ, by the strip for the 4 per cent solution. The mother solution, according to the negative, transmitted very weakly from about 0.538 μ to the end of the field of view of the spectrograph. Eye observations recorded qualitatively the facts revealed by the negative, and also supplemented the latter by giving data for the red end of the spectrum. The depth of cell was, as formerly, 0.24 cm. All light transmitted by the mother solution was very weak, yet the transmission in the red was relatively intense, as compared with that in the yellow and green. More specifically, transmission began at about 0.725 μ, rose to a maximum at 0.653 μ, and then fell to a very small value in the neighborhood of 0.598 μ. Faint light could be observed from 0.598 μ to about 0.518 μ. At the latter wave length absorption became complete. The spectrum transmitted by the 4 per cent solution was similar to that of the mother solution. The yellow and green regions, however, were somewhat stronger, but the blue was very much weakened. The contrast between a relatively bright region of transmission, and a weak region at the more refrangible side of the former, gradually disappeared as the quantity of water in the solutions decreased. The gradations were shown very well by the corresponding negative strips of the spectrogram. For the solution which contained the greatest amount of water the spectrum began near 0.758 μ. The complete series of eye observations showed that the visible end of the absorption band, whose center was in the infra-red, moved towards this region as the percentage of water in the solutions increased.

A series of solutions could not be prepared from copper bromide and acetone, since the latter oxidizes the acetone, and is itself reduced to the cuprous condition and immediately precipitated. The spectrograms, which were taken for the purpose of comparing with one another the absorption spectra of certain solutions of copper bromide in water, in methyl alcohol and ethyl alcohol, are reproduced as Plates XIV(*a*) and XIV(*b*).

Since the mother solutions were too opaque to give satisfactory spectrograms, each was diluted with the proper solvent. The concentrations of the solutions of copper bromide in water, in methyl alcohol and ethyl alcohol were, respectively, 0.874, 0.036, 0.032. When placed in the cell at a depth of 0.24 cm., the solutions in the order given above, were green, light yellow and yellow with a brownish tinge. For Plate XIV(*a*) the strip adjacent to the numbered scale corresponds to the solution in methyl alcohol. The middle strip pertains to the solution in methyl alcohol, and the strip nearest to the spark spectrum corresponds to the aqueous solution. The strip for the ethyl alcohol solution showed that transmission began at about 0.445 μ, and remained comparatively weak as far as 0.527 μ. From this latter point on towards the red, transmission was relatively strong. The negative strip pertaining to the solution in methyl alcohol showed that transmission began near 0.419 μ, and continued intense as far as the limit of sensibility of the photographic film. The negative strip corresponding to the aqueous solution showed that transmisssion began at 0.403 μ, and remained strong to the limit set by the absence of sensitiveness of the film to orange light. The fact that the middle strip extends beyond the adjacent strips at their less refrangible ends, shows that slight general absorption of the orange was exerted by the solutions in ethyl alcohol and in water.

The negative for Plate XIV(*b*) was taken with a Cramer trichromatic plate. The cell depth was 1.75 cm., and each exposure to the light from the Nernst filament was 2 minutes. At this depth the solution of ethyl alcohol had a deep, dull brown color. The solution in methyl alcohol was a deep brownish yellow. The aqueous solution was dark green. The strip adjacent to the scales corresponds to the aqueous solution, the middle strip pertaining to the solution in methyl alcohol as solvent. The negative showed that the ethyl alcohol solution transmitted very weakly from 0.554 μ to the end of the plate. The photographic maximum of transmission was near 0.595 μ. The middle strip showed that the methyl alcohol solution began to transmit at about 0.480 μ, and that transmission was practically complete from 0.510 μ

to the end of the field of view of the spectrograph. The negative strip next to the spark spectrum showed that the aqueous solution began to transmit at 0.455 μ, but the brightness of the transmitted light increased very slowly to a maximum in the vicinity of 0.556 μ. Transmission ended at 0.603 μ.

The solutions in question were studied with the spectroscope, the cell having the same depth as for Plate XIV(*b*). The solution in methyl alcohol transmitted red and orange fairly well, but yellow and greenish yellow rather faintly. The spectrum began at 0.705 μ, rose to a maximum at 0.640 μ and then decreased to a region of very weak transmission, which extended from 0.588 μ to 0.543 μ. The methyl alcohol solution transmitted red and orange tolerably well, and yellow quite intensely. The spectrum was relatively weak in the blue. Transmission began at about 0.716 μ, and reached its full value in the neighborhood of 0.610 μ. The intensity decreased from about half its maximum value at 0.525 μ to complete absorption at 0.481 μ. The spectrum of copper bromide in methyl alcohol was very much more intense than that for the solution of the same salt in ethyl alcohol. For the aqueous solution transmission began near 0.636 μ, rose to a maximum at about 0.580 μ, and maintained a comparatively small intensity from 0.520 μ to 0.470 μ. The entire spectrum was a good deal weaker than the spectrum of the methyl alcohol solution, and yet appreciably more intense than the solution in ethyl alcohol.

General Conclusions from Spectrographic Work.

That the absorption spectra of solutions, such as those described in this and in the preceding paper, both separately and when mixed, can throw light on the question of hydration, is readily seen from the following considerations, some of which have already been pointed out:

The phenomenon of absorption, as presented by solutions, is one of resonance. The energy of a vibration of given period, will be absorbed to the greatest extent by a system whose natural period of vibration is most nearly equal to its own.

The period of vibration of a dissolved particle will be *greatly affected by the condensation around it of water molecules—by the formation of hydrates.*

The *more complex the hydrate* in combination with the dissolved particle, the more the vibrations of the particle would be interfered with and, consequently, the *smaller the number of wave lengths with which it would be able to vibrate in resonance.* Therefore, the *solution in which the hydrates were the most complex would have the narrowest absorption bands.*

This conclusion can readily be tested experimentally by means of the absorption spectra. Earlier work in this laboratory has shown that *the more dilute the solution, the more complex the hydrate existing in the solution.* The more dilute solutions should, then, show narrower absorption bands than the more concentrated.

This is shown by Plate II. (p. 162), which represents the spectrograms of a series of solutions of cobalt chloride. The most dilute solution is nearest the numbered scale, and the concentration increases as we go down the plate from the scale. The absorption bands widen out rapidly as the concentration of the solution increases.

Exactly the same relation is brought out by Plate V. (p. 166) for aqueous solutions of copper chloride. The absorption bands widen as the concentration increases; and similar relations come out equally well for copper bromide in water. These are shown by Plate VI. (p. 170), the absorption bands widening rapidly with increasing concentration.

If a solution of a *strong dehydrating agent,* such as calcium chloride or aluminium chloride, is added to an aqueous solution of, say, cobalt chloride, some of the water will be removed from the latter and its particles would be freer to vibrate. The addition of *more and more of the dehydrating agent should, therefore, produce a widening of the absorption bands,* just as increasing the concentration of a solution causes the absorption bands to widen out.

That such is the case is shown by Plate VIII. (p. 172). The solution next to the scale represents pure cobalt chloride. The following strips correspond to solutions containing more and more calcium chloride, the amount of cobalt chloride present remaining constant. It will be observed that the absorption bands widen as the amount of calcium chloride present increases.

The same fact is shown by Plate XIII. (p. 194). The strip next to the scale corresponds to a solution of pure copper chloride, and the succeeding strips to solutions containing more and more calcium chloride. The absorption bands widen with marked regularity.

The absorption spectra of solutions of copper chloride, to which more and more aluminium chloride is added, are shown in Plate XVII. (p. 216), the absorption bands widening regularly with increase in the amount of aluminium chloride.

It will be observed that in Plates VIII., XIII. and XVII. the bands widen, *while the amount of colored salt present remains constant*, and the amount of the colorless salt increases. This shows that there is *no necessary relation between the widening of the bands and the concentration of the colored salt as such.* In order that the bands should widen with increasing concentration, when only the colored salt is present, there must be a change in the hydration of the colored salt.

Let us now turn to solutions of cobalt chloride, copper chloride and copper bromide in such non-aqueous solvents as methyl alcohol, ethyl alcohol and acetone. Take a solution of cobalt chloride in methyl alcohol. In such a solution there can be no hydrate present, since there is no water present; and there is no evidence that the dissolved substance combines with any appreciable amount of the methyl alcohol. In such a solution the dissolved substance, not being weighted down by anything combined with it, would be freest to vibrate in resonance with a large number of wave lengths. The absorption bands should, therefore, be relatively broad. As more and more water is added to the alcoholic solution, the dissolved substance should form more and more complex hydrates, and would be less and less free to vibrate in resonance with any large number of wave lengths. The absorption bands should, therefore, become narrower and narrower as the amount of water present becomes greater and greater.

That such is the case is shown by Plate II. (p. 248). The strip most widely removed from the numbered scale represents the absorption spectrum of cobalt chloride in anhydrous methyl alcohol; and here the bands are the widest. The succeeding strips approaching the scale, represent the solutions of cobalt chloride in methyl alcohol to which more and more water is added. The strip next to the numbered scale corresponds to the maximum amount of water. It will be observed that as the amount of water increases, the absorption bands become narrower and narrower, and are narrowest for the solution containing the maximum amount of water.

The same relation is shown by copper chloride in methyl alcohol. In Plate VII. the lowest strip is the absorption spectrum in pure alcohol. There the absorption is greatest. As more and more water is added to the alcoholic solution, a more and more complex hydrate is formed, which hinders the vibration of the dissolved substance. The absorption bands, therefore, become narrower and narrower as the amount of water present increases.

A study of copper chloride in ethyl alcohol confirms the above conclusion. The strip most remote from the numbered scale of Plate VIII. (p. 259) represents the solution in pure ethyl alcohol. The dissolved molecules are not combined with any appreciable amount of the solvent, and they can, therefore, vibrate freely. They vibrate in resonance with a very large number of wave lengths, and the absorption bands extend nearly across the entire spectrum. As more and more water is added, the molecules of the copper salt become hydrated to a greater and greater extent, and their absorption becomes less and less. This is shown by the rapid narrowing of the absorption bands as more and more water is added to the alcoholic solution.

The above relations repeat themselves for copper chloride in acetone Plate IX. (p. 260). The solution of the pure acetone has the widest bands or greatest absorption, as is shown at the bottom of the plate. The amount of absorption diminishes as the amount of water increases. Indeed, one band entirely disappears after the amount of water present reaches a certain value. Plates XI. and XII. (pp. 263, 264) bring out the same facts for copper bromide in methyl alcohol and in ethyl alcohol. The strips most widely removed from the numbered scales represent the absorption spectra in the pure alcohols. The successive strips, as we approach the scale, represent the addition of more and more water. The hydrates are becoming more and more complex, and the power to vibrate in resonance with many wave lengths less and less. Consequently, the absorption bands are continually becoming narrower and narrower.

If we take into account all of the above evidence from spectroscopic investigation, it seems fair to conclude that this argues very satisfactorily in favor of the present conception of hydrates in aqueous solutions. Attention is called especially to Plates VIII., XIII., and XVII. (pp. 172–194), which show that the widening of the bands is not a function simply of the number of molecules of the colored salt that is present. In order that the absorption bands should widen simply by increasing the concentration of the colored salt alone, it is necessary, as has been shown, for the *hydration of the colored salt to undergo change.* The evidence furnished by solutions in non-aqueous solvents, on addition of water, in favor of the hydrate conception, seems quite as convincing as that obtained from solutions in water itself.

In conclusion, we wish to express our thanks to the Physical Department of this University, for making possible the favorable conditions under which this work was carried out.

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PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
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Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XIV.—STUDIES ON THE SOILS FROM THE NORTHERN PORTION OF THE GREAT PLAINS REGION: THE DISTRIBUTION OF CARBONATES ON THE SECOND STEPPE.

By Frederick J. Alway and Guy R. McDole.

It has been shown by Hilgard[1] that one of the characteristics of the soils of arid regions is the large content of carbonates of calcium and magnesium compared with the soils of humid localities. In the absence of sufficient rainfall to cause percolation through the subsoil, the carbonates, which are dissolved from the surface soil by the rains, accumulate in the subsoil where the last portions of the water are absorbed by the plant roots. It has been found at Rothamsted that the annual loss of calcium carbonate in the drainage water from unmanured plots amounts to about 1000 pounds per acre.[2] At this rate about 200 years would be sufficient for the removal of all the calcium carbonate from 1 foot of subsoil of one of the most important soil types of the steppe, while at the end of 2000 years practically all the calcium carbonate within reach of plant roots would have been removed. Even in the case of the type of soil best supplied with carbonates, 7000 years would have completed the leaching. Assuming that the soils of eastern and western Canada, all of which are of glacial origin, were at first equally rich in carbonates, sufficient time has elapsed since the glacial period to account for the disappearance of these compounds from the soils of the former.

Determinations of carbon dioxide were made in the case of all our samples that formed complete sets to the depth of 6 feet. The 72 samples, the analysis of which is given in Table I., show the distribution as well as the total amount of carbonates occurring in the 2 most fertile types of soil on the second steppe. At many other places than those from which the ones mentioned below were taken, samples of subsoil were obtained, and in all cases were found to contain from 1.50 to 12.00 per cent of carbon dioxide. We find that, in general, there is a tendency for the amount of carbonates to reach a maximum in the second and third foot, or in the portion of subsoil between the second and the fifth foot. In all cases the surface soil is distinctly poorer in carbonates than the subsoil. The most marked regularity in the results, however, is the direct relation between the amount of carbonates and the hygroscopic coefficient of the subsoils. A large content of carbonates is associated with a low hygroscopic coefficient, as is well shown in Table II., in which the results are arranged in the order of the percentage of carbon dioxide.

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[1] Cal. Agr. Expt. Station, Report 1892–94, p. 100.

[2] Hall: Rothamsted Expt., p. 239 (1905).

All samples were obtained by means of a 1.5 inch augur. As each of the samples represents a whole foot section, some of them consist of a mixture of two types of subsoil, where both occurred within the same foot section. The hygroscopic coefficient[1] was determined by exposing a thin layer, 1 mm., of the soil to an atmosphere saturated with water vapor, for 13 hours and afterwards drying at 100° for 24 hours. The coefficient expresses the weight of water held by 100 grams of dry soil. All the fields from which the samples were taken had been under cultivation for many years, with the exception of J, K and L, which were still in virgin prairie. L formed a depression into which the water from the higher (3–6 feet) land of J on the one side and K on the other, each half a mile distant, ran off during very heavy rains. On account of this collection of water over its surface there had been more opportunity for seepage, which evidently had reduced the total amount of carbonate as well as that in the second foot. This field bore a much heavier growth of grass than the adjacent higher land.

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[1] Cal. Agr. Expt. Station, Circular No. 6, p. 13 (1903).

Table I.

Series letter of field.	Locality.	Series number of sample.	Depth of foot section in feet.	Percentage of CO_2.	Hygroscopic coefficient.	Temperature of observation.	Character of soil.
A	Indian Head	1	1	0.63	10.0	15	Lacustral clay.
		2	2	2.57	10.9	"	" "
		3	3	2.23	10.9	"	" "
		4	4	9.46	4.7	"	Boulder clay.
		5	5	9.25	4.9	"	" "
		6	6	9.31	4.5	"	" "
B	Indian Head	7	1	0.42	10.9	"	Lacustral clay.
		8	2	3.38	9.7	17	Lacust. clay and boulder clay.
		9	3	10.26	4.8	"	Boulder clay.
		10	4	8.28	5.4	"	" "
		11	5	8.35	5.5	"	" "
		12	6	8.17	4.4	"	" "
C	Indian Head	13	1	0.21	11.8	20	Lacustral clay.
		14	2	1.84	10.8	"	" "
		15	3	10.20	4.7	"	Boulder clay.
		16	4	8.65	4.4	"	" "
		17	5	9.00	4.4	"	" "
		18	6	8.00	5.2	"	" "
D	Indian Head	19	1	1.70	9.6	10	Boulder clay.
		20	2	9.12	5.6	"	" "
		21	3	11.82	5.6	"	" "
		22	4	9.75	4.5	"	" "
		23	5	6.80	5.8	"	Boulder clay and lacustral clay.
		24	6	6.67	8.7	"	Lacust. clay and boulder clay.
E	Indian Head	25	1	0.65	12.8	10	Lacustral clay.
		26	2	2.24	13.1	"	" "
		27	3	3.80	12.3	"	" "
		28	4	8.60	5.5	15	Boulder clay.
		29	5	8.86	5.5	"	" "
		30	6	7.66	6.6	"	" " and lacustral clay.

Table I—(continued).

Series letter of field.	Locality.	Series number of sample.	Depth of foot section in feet.	Percentage of CO_2.	Hygroscopic coefficient.	Temperature of observation.	Character of soil.
F	Indian Head	31	1	0.46	11.4	12	Lacust. clay and boulder clay.
		32	2	9.51	5.9	"	Boulder clay.
		33	3	9.93	4.6	"	" "
		34	4	8.00	4.3	"	" "
		35	5	7.53	3.9	"	" "
		36	6	7.28	5.0	"	" "
G	Moose Jaw	37	1	Sample lost.			
		38	2	2.22	12.8	15	Lacustral clay.
		39	3	3.21	11.8	"	" "
		40	4	2.87	11.7	"	" "
		41	5	2.77	10.9	"	" "
		42	6	2.70	12.9	"	" "
H	Moose Jaw	43	1	1.28	13.9	17	Lacustral clay.
		44	2	2.05	13.2	"	" "
		45	3	2.25	11.7	"	" "
		46	4	1.97	11.8	"	" "
		47	5	2.96	11.9	"	" "
		48	6	3.19	11.5	"	" "
I	Moose Jaw	49	1	0.83	13.8	11	" "
		50	2	3.04	12.7	"	" "
		51	3	2.97	11.7	"	" "
		52	4	3.00	11.9	16	" "
		53	5	3.18	11.7	"	" "
		54	6	2.63	11.1	"	" "
J	Belle Plaine	55	1	1.25	14.7	13	" "
		56	2	2.58	14.1	"	" "
		57	3	2.50	13.8	"	" "
		58	4	2.36	13.5	14	" "
		59	5	1.90	14.5	"	" "
		60	6	2.23	14.5	"	" "
K	Belle Plaine	61	1	0.82	13.8	14	" "
		62	2	2.63	12.5	"	" "
		63	3	2.34	12.4	"	" "

Table I—(continued).

Series letter of field.	Locality.	Series number of sample.	Depth of foot section in feet.	Percentage of CO_2.	Hygroscopic coefficient.	Temperature of observation.	Character of soil.
K	Belle Plaine	64	4	2.97	11.9	14	Lacustral clay.
		65	5	2.42	13.7	"	" "
		66	6	1.41	14.9	"	" "
L	Belle Plaine	67	1	0.64	14.8	11	" "
		68	2	1.25	14.5	"	" "
		69	3	2.09	14.6	"	" "
		70	4	1.90	14.1	"	" "
		71	5	1.80	13.6	12	" "
		72	6	2.51	13.7	"	" "

Table II.

Series number of sample.	Percentage of CO_2.	Hygroscopic coefficient.	Series letter of field.	Locality.	Character of soil.	Depth of foot section in feet.
13	0.21	11.8	C	I. H.	Lacustral clay.	1
7	0.42	10.9	B	"	" "	1
31	0.46	11.4	F	"	" " and boulder clay	1
1	0.63	10.0	A	"	" "	1
67	0.64	14.8	L	B. P.	" "	1
25	0.65	12.8	E	I. H.	" "	1
61	0.82	13.6	K	B. P.	" "	1
49	0.83	13.8	I	M. J.	" "	1
55	1.25	14.7	J	B. P.	" "	1
68	1.25	14.5	L	"	" "	2
43	1.28	13.9	H	M. J.	"	1
66	1.41	14.9	K	B. P.	"	6
19	1.70	9.6	D	I. H.	Boulder clay.	1
71	1.80	13.6	L	B. P.	Lacustral clay.	5
14	1.84	10.8	C	I. H.	" "	2
59	1.90	14.6	J	B. P.	" "	5
70	1.90	14.1	L	"	" "	4
46	1.97	11.8	H	M. J.	" "	4
44	2.05	13.2	"	"	" "	2

Table II—(continued).

Series number of sample.	Percentage of CO_2.	Hygroscopic coefficient.	Series letter of field.	Locality.	Character of soil.	Depth of foot section in feet.
69	2.09	14.6	L	B. P.	Lacustral clay	3
38	2.22	12.8	G	M. J.	" "	2
3	2.23	10.9	A	I. H.	" "	3
60	2.23	14.5	J	B. P.	" "	6
26	2.24	13.1	E	I. H.	" "	2
45	2.25	11.7	H	M. J.	" "	3
58	2.36	13.6	J	B. P.	" "	4
65	2.42	13.7	K	"	" "	5
57	2.50	13.9	J	"	" "	3
72	2.51	13.7	L	"	" "	6
2	2.57	10.9	A	I. H.	" "	2
56	2.58	14.2	J	B. P.	" "	2
54	2.63	11.1	I	M. J.	" "	6
62	2.63	12.5	K	B. P.	" "	2
42	2.70	12.9	G	M. J.	" "	6
41	2.77	10.9	"	"	" "	5
63	2.84	12.4	K	B. P.	" "	3
40	2.87	11.7	G	M. J.	" "	4
47	2.96	11.9	H	"	" "	5
51	2.97	11.7	I	"	" "	3
64	2.97	11.9	K	B. P.	" "	4
52	3.00	11.9	I	M. J.	" "	4
50	3.04	12.7	"	"	" "	2
53	3.18	11.7	"	"	" "	5
48	3.19	11.5	H	"	" "	6
39	3.21	11.8	G	"	" "	3
8	3.38	9.7	B	I. H.	Lacustral clay and boulder clay	2
27	3.80	12.3	E	"	Lacustral clay.	3
24	6.67	8.7	D	"	Lacustral clay and boulder clay	6
36	7.28	5.0	F	"	Boulder clay.	6
35	7.53	3.9	"	"	" "	5
30	7.66	6.6	E	"	Lacustral clay and boulder clay	6
34	8.00	4.3	F	"	Boulder clay.	4
18	8.00	5.2	C	"	" "	6
12	8.17	4.4	B	"	" "	6
10	8.28	5.4	"	"	" "	4
11	8.35	5.5	"	"	" "	5
28	8.60	5.4	E	"	" "	4

Table II—(continued).

Series number of sample.	Percentage of CO_2.	Hygroscopic coefficient.	Series letter of field.	Locality.	Character of soil.	Depth of foot section in feet.
16	8.65	4.4	C	I. H.	Boulder clay	4
29	8.86	5.5	E	"	" "	5
17	9.00	4.4	C	"	" "	5
20	9.12	6.6	D	"	" "	2
5	9.25	4.9	A	"	" "	5
6	9.31	4.5	"	"	" "	6
4	9.46	4.7	"	"	" "	4
32	9.56	5.9	F	"	" "	2
22	9.75	5.6	D	"	" "	4
33	9.93	4.6	F	"	" "	3
15	10.20	4.7	C	"	" "	3
9	10.26	4.8	B	"	" "	3
21	11.82	5.8	D	"	" "	3

The amount of carbonates in the surface soils is, in all cases, less than that in the subsoil. The subsoil, judged by the content of carbon dioxide, is of 2 distinct types, the one carrying from 7.5 to 12 per cent and the other from 1.25 to 4.0 per cent. These two types of subsoil differ in physical as well as in chemical properties. The first, boulder clay, carries stones and boulders, while in the second, a clay of lacustral origin, only an occasional small stone is found. The former readily disintegrates in contact with water, from 1 to 3 hours' boiling being sufficient to reduce it to clean, single grains, as observed under the microscope, while the latter, when treated with water, breaks up into small aggregations, which, when rubbed with a stirring rod, become like putty, and which require from 30 to 36 hours' boiling with water to completely resolve them into their individual soil particles. The till or boulder clay possesses a much lighter color, both in the wet and in the dry condition, than the lacustral clay. The dried lumps of the former can be crushed between the thumb and finger, while those of the latter cannot. As is shown by the table of mechanical analysis, the till is much richer in sand and poorer in clay particles than the lacustral deposit; the proportion of silt in the two is about the same. The difference in appearance of the two types of soil, when removed from fields in which a crop of grass or some cereal has just reached maturity, is very marked, the till being brought to the surface by an augur in the form of a powder, resembling wood ashes, while the other forms a more or less coherent mass of small aggregations. One of the most important and characteristic properties in which the 2 types differ is the hygroscopic coefficient of the subsoil. The surface soil, on account of the humus it contains, possesses a high coefficient, no matter to which type it belongs. In the case of the subsoils that of the till has a value between 3.9 and 6.0, and that of the lacustral clay lies between 10.3 and 14.7. The samples, whose coefficient lay between 5.8 and 10.8, were very few in number, *viz.*, 8, 24 and 30; a careful examination showed that they consisted of mixtures of the 2 types, as was to be expected from the percentage of carbon dioxide.

Table III.

Mechanical Analysis of Specimens of the Two Soil Types.

	Series No. 9. Boulder clay. Per cent.	Series No. 26. Lacustral clay. Per cent.
Gravel, 2.0 to 1.00 mm.	1.7	0.0
Coarse sand, 1.0 to 0.5 mm.	5.2	0.01
Medium sand, 0.5 to 0.25 mm.	5.6	0.01
Fine sand, 0.25 to 0.10 mm.	14.1	2.2
Very fine sand, 0.10 to 0.05 mm.	12.3	6.7
Coarse silt, 0.05 to 0.016 mm.	16.2	19.0
Fine silt, 0.016 to 0.005 mm.	19.5	22.6
Clay, 0.005 to ?	26.1	48.2
Total	100.7	98.8

All the samples from Moose Jaw and Belle Plaine are of lacustral clay; at Indian Head, fields D and F, at the spots where borings were made, are of boulder clay, while fields A, B, C and E are of lacustral clay to a depth of from 1.5 to 3 feet, below which is boulder clay. In both D and E a layer of rather stiff clay, resembling the lacustral deposit, was found at a depth of about 5 feet. In the tables this is referred to as lacustral clay. As its resemblance to the surface deposit was recognized only after the hygroscopic coefficient and carbon dioxide had been determined, no careful examination was made in the field. In most of the fields examined on the Indian Head Experimental Farm the surface soil seemed to consist of a mixture of the 2 types. This is probably due to a combination of 3 causes, *viz.*, (1) high winds, which blow soil from the surface of one type over the surface of the other; (2) the action of the plow where the layer of lacustral clay is very shallow; (3) the work of burrowing animals which carry boulder clay subsoil to the surface and deposit it upon the lacustral clay.

Mr. C. E. Vail, of this laboratory, made carbon doxide determinations of the 4 portions into which the finer material of the till may readily be separated by mechanical analysis. As was to be expected, very little carbon dioxide was obtained from the clay portion.

	Sands.	Coarse silt.	Fine silt.	Clay.
Per cent of CO_2	4.59	12.41	9.08	0.29

Summary.

1. All soils from the second steppe are well provided with carbonates, the subsoils containing more than the corresponding surface soils.
2. Subsoils of boulder clay are much richer in carbonates than those composed of clay of lacustral origin.
3. The carbonates are present chiefly in the soil grains of intermediate size, *viz.*, the silts.
4. A high percentage of carbonates is associated with a low hygroscopic coefficient.

UNIVERSITY PLACE,
NEBRASKA,
July, 1906.

NOTE.

The Generation of Oxygen from Sodium Peroxide.

In a recent note[1] a method is described for lessening the violence of the action of water on fused sodium peroxide in the generation of oxygen. Sodium sulphate, or carbonate crystals, mixed with the peroxide, supply the necessary water. On warming, oxygen is regularly evolved. A similar way of overcoming the difficulty, that may, in certain cases, prove more convenient, is to use an aqueous solution of caustic alkali instead of water alone. Place a lump of the peroxide on a piece of copper gauze, in a dry, round-bottomed flask and add, by means of a dropping funnel, the alkali solution of strength about 1:1. I have used exhausted nitrometer solution. Oxygen is evolved without the need of external heating, and the rate of evolution is sufficiently regular for most purposes.

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[1] THIS JOURNAL, **37**, 106 (1907).

GEORGE H. BURROWS.

UNIVERSITY OF VERMONT.

OBITUARY.

DMITRI IVANOWITSH MENDELÉEFF.

The death of Mendeléeff, in his seventy-third year, has just been announced.

Dmitri Ivanowitsh Mendeléeff was born February 7, 1834, at Tobolsk, Siberia, and died in St. Petersburg, February 2, 1907. He was educated at the gymnasium at Tobolsk and in the scientific department of the Pedagogical Institute at St. Petersburg, an institution for the training of gymnasium teachers. He had a brief period of activity as a teacher, and then took the degree of *Magister Chemiae* at the St. Petersburg University, in 1856. After a stay of 2 years at Heidelburg, he became Professor of Chemistry at the Technological Institute at St. Petersburg and, in 1866, was made Professor of Chemistry at the University of St. Petersburg.

Mendeléeff was a very prolific writer and worked in every field of chemical science. He contributed to our knowledge of mineralogy and chemical geology and carried out several noteworthy researches in organic chemistry. In 1863 he published the first Russian encyclopedia of Technical Chemistry. His influence on the Russian petroleum industry has been all-important. Twenty years ago the petroleum industry of Baku was a monopoly with limited trade and unprogressive management. Thanks largely to the action of Mendeléeff, both on the platform and in the press, the exploitation of this boundless supply was thrown open to the world, with results of the greatest industrial and political importance.

Mendeléeff's reputation rests mainly on his contributions to physical chemistry and to chemical philosophy; among the more important of these are his researches on Specific Volumes, which were stimulated by the work of Kopp, commenced while he was a student in 1855 and continued until

1870; his work on Contact Action, on Fractional Distillation, on the Heat of Combustion of Organic Substances, and on Solution. Much of his activity since 1871 has been given to extended work on the Elasticity of Gases, in collaboration with several of his pupils. Portions only of this work have been published.

Mendeléeff was noted as an inspiring teacher. Two generations of Russian chemists owe their training to him. His treatise on Organic Chemistry was the standard work of its time; his "Principles of Chemistry," first printed in 1869, has passed through 7 editions in Russia and 3 in England. It is a veritable treasure-house of ideas, from which investigators have constantly borrowed suggestions for new lines of research. In it Mendeléeff developed the great generalization known under the name of the "Periodic Law."

It is as the author and expounder of the Periodic Law that Mendeléeff's name is familiar to every student of chemistry, and doubtless his fame in the future will rest chiefly on this basis. He first called attention to the principles on which this law is based in a paper read to the Russian Chemical Society, in 1869. From that time to the present day many chemists, in lectures and in print, have taught that the law can only find its explanation in the Pythagorean theory of an ultimate unity of matter. It is well to again call the reader's attention to what Mendeléeff himself says on this subject.

In his Faraday Lecture, delivered to the English Chemical Society, June 4, 1889, Mendeléeff has indicated the lines on which the evolution of this theory proceeded; that it was based wholly on experiment, that without the knowledge of certain data it could not possibly have been discovered, that with this knowledge its appearance is natural and intelligible. In Mendeléeff's words "the law was the direct outcome of the stock of generalizations of established facts which had accumulated by the end of the decade 1860–1870." He indicates the bearing of the law on the doctrine of constant valency, and on the conception of a primordial matter and continues, "the Periodic Law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of an unique matter, and it has no historical connection with that relic of the torments of classical thought; and, therefore, it affords no more indication of the unity of matter, or of the compound nature of the elements, than do the laws of Avogadro and Gerhardt, or the law of specific heats, or even the conclusions of spectrum analysis."

Mendeléeff was the recipient of honors throughout the chemical world. To mention only a few, he was Honorary Member of the Chemical societies of Germany and America; Foreign Member of the Chemical Society (London) and of the Royal Society; Foreign Associate of the National Academy of Sciences; Member of the Royal Academy of Sciences, Crakow; Honorary President of the Russian Physical-Chemical Society. He received the Davy and Copley medals from the Royal Society and the Faraday medal from the Chemical Society.

The reader who wishes to learn more of Mendeléeff's lifework should turn to Thorpe's excellent study in "Essays in Historical Chemistry," from which most of the material for this notice is taken.

REPORT.

Oxides of the Alkali Metals.

Some of the higher oxides of the alkali metals have been previously studied and are well known. Recently, Rengade[1] has extended our knowledge of these oxides.

The oxides of caesium, rubidium, potassium and sodium, of the composition M_2O, corresponding to the common hydroxides, MOH, hitherto have remained unknown, all attempts to isolate them having failed. Beketoff[2] claims to have made rubidium oxide, Rb_2O, by oxidizing rubidium in a current of air to a mixture of oxides, and reducing this mixture to the monoxide by heating it with rubidium in an atmosphere of nitrogen. Later observers could not confirm these results. Rengade[3] has prepared the oxides by a simple method. He brings a weighed amount of metal into a tube, creates a vacuum in the tube and admits a measured volume of oxygen, which is less than the calculated volume required to oxidize the metal to the oxide, M_2O. After combination, the excess of metal is distilled off, leaving the non-volatile oxide. Caesium reacts violently with oxygen and becomes incandescent, rubidium less violently, while with potassium and sodium heat was required to start the reaction.

Caesium oxide, Cs_2O, is an orange-red, crystalline substance; when heated in a vacuum the color changes, with increasing heat, to carmine-red, to purple, and to black at 150°. On cooling, the color phases are reversed. The oxide reacts violently with water, $Cs_2O + H_2O = 2CsOH$. Between 400°

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[1] C. r., **140**, 1536; **142**, 1533.

[2] Beketoff: Bull. Acad. St. Petersburg, **1**, 174 (1894).

[3] Rengade: C. r., **143**, 592, 1152.

and 500° the monoxide decomposes into caesium dioxide and caesium, $2Cs_2O = Cs_2O_2 + 2Cs$.

The last reference given above is a brief note announcing the preparation of the monoxides of rubidium, potassium and sodium. The first is yellow, the last two are white.

E. RENOUF.

REVIEWS.

CHEMICAL ABSTRACTS. Edited by W. A. NOYES and C. E. WATERS, Easton, Pa.: American Chemical Society. Vol. I, No. 1, January 1. 1907. Published semi-monthly. Price, $6.00 per annum.

The appearance of a journal, in the English language, devoted wholly to abstracts of chemical papers, is a most noteworthy event and one that may have an extremely important influence on chemistry throughout the world. It is a distinct challenge to German leadership.

The first thought which its appearance brings is one of regret that it has not been found possible to arrange for an abstract journal issued jointly by the Chemical Society (London), the Society of Chemical Industry and the American Chemical Society, so as to prevent the extravagant waste of time, money and energy involved in the duplication of abstracts. It is tolerably well known that negotiations with this object were opened by the American Society, and that their failure was not due to any lack of effort on its part.

In judging of the degree of success which the editors have attained, it is necessary to compare "Chemical Abstracts" with the "Chemisches Central-Blatt," because the abstracts in the journals of the two English societies do not profess to be complete, but to deal only with pure and applied chemistry, respectively. The "Central-Blatt" is issued weekly and costs $16.00, but, in all probability, the price will be again raised next year. It is not complete and very many abbreviations are used. It is, of course, in the German language, and is subscribed for by only one-half (1600) of the members of the German Chemical Society. As stated above, "Chemical Abstracts" is issued semi-monthly, costs $6.00, is more complete than the German journal, the contents are free from irritating contractions, and are much more conveniently arranged. It is issued to all the members of the American Chemical Society, who now number more than 3000. In these circumstances it is difficult to see why English-speaking chemists should continue to subscribe to the "Central-Blatt." Under the Editor and Associate Editor, there are over 120 Sectional

Editors and Abstractors in charge of the following departments: APPARATUS; RADIOACTIVITY; ELECTROCHEMISTRY; PHOTOGRAPHY; INORGANIC CHEMISTRY; ANALYTICAL CHEMISTRY; MINERALOGICAL AND GEOLOGICAL CHEMISTRY; METALLURGY; ORGANIC CHEMISTRY; BIOLOGICAL CHEMISTRY; FOODS; NUTRITION; WATER, SEWAGE, SANITATION; SOILS AND FERTILIZERS; FERMENTED AND DISTILLED LIQUORS; PHARMACEUTICAL CHEMISTRY; ACIDS, ALKALIES, SALTS; GLASS AND POTTERY; FUEL, GAS, COKE; CELLULOSE AND PAPER; EXPLOSIVES; DYES, BLEACHING AND TEXTILE FABRICS; PIGMENTS, RESINS, VARNISHES, INDIA RUBBER; FATS, FATTY OILS AND SOAP; SUGAR, STARCH AND GUMS; LEATHER; PATENTS.

It will be seen from the above brief outline that the American Chemical Society and the Editorial Staff have done their part well; it only remains for English-speaking chemists all over the world to show their appreciation of the efforts which have been made by subscribing for "Chemical Abstracts," or, better still, by becoming members of the American Chemical Society; the dues are only $8.00 per annum and members receive, without further charge, both the Society's "Journal" and "Chemical Abstracts." J. B. T.

LA GRANDE INDUSTRIE CHIMIQUE. Les Acides. Chlorhydrique, Azotique, Sulfurique (sulphate de sodium et eau régale), et les Chlorures décolorants (eau de Javel, eau de Labarraque, chlorure de chaux) par H. PÉCHEUX, Professeur de chimie a l'école nationale d'arts et métiers d'Aix. Paris: J. B. Baillière et Fils. 1906. pp. 96. Price, $1.50.

This is one of a series of publications on chemical industry. The present volume would be a useful little handbook had technical chemistry not advanced in the last 20 years. The text and illustrations are satisfactory as far as older methods are concerned.

In a review of the preceding volume of the series,[1] it was pronounced incomprehensible that a respectable publisher should dare offer the volume to the public, but it was suggested that it might be an unrevised reprint of an older work; that this excuse cannot be offered is shown by the description, in the present book, of Knietsch's contact process for making sulphuric acid.

The omissions in this volume are as remarkable as in the preceding one. The action of sulphuric acid on salt is the only technical process given for making hydrochloric acid. No mention is made of electrolytic methods for preparing chlorine or for making bleaching powder! The following table[1] gives the relative percentage of bleaching powder made at the present time by the electrolytic and the old methods in different countries.

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[1] THIS JOURNAL, 36, 220.

	Electrolysis. Per cent.	Older methods. Per cent.
Germany	65	35
England	18	82
France	19	81
United States	100	0
Austria	66	34
Spain and Italy	100	0
Russia	55	45
Belgium	54	46

Considering that 19 per cent of French bleaching powder is made by the electrolytic method, failure to mention the process needs no comment. E. R.

ANLEITUNG ZUR VEREINFACHTEN ELEMENTARANALYSE. By PROFESSOR M. DENNSTEDT, Direktor des Chemischen Staats-Laboratoriums in Hamburg. Second Edition. Hamburg: Otto Meissner. 1906. pp. 100. Price, M. 2.40.

Dr. Dennstedt's efforts on behalf of simplified elementary analysis are at last beginning to bear fruit; during the past 2 or 3 years hardly a month has elapsed without the publication of at least one paper on the subject, and some of the processes which have been suggested are actually in use in a few university laboratories! As is well known, Dennstedt's method consists, primarily, in the employment of finely divided platinum instead of copper oxide for the oxidation of volatile material. This is contained in a short tube, and effects a relatively enormous saving of gas and time, the latter being especially marked when the duplex oxygen supply is used. The experience of the method, gained since the book was first published, has been utilized, to amend, in the present edition, the descriptions of apparatus and procedure and to introduce a number of improvements in detail, but, fundamentally, the process has not been either complicated or modified.

Professor Dennstedt is to be congratulated on the success of the first edition of his book, and it may be confidently anticipated that an even greater measure of favorable recognition will be accorded to the present issue. In the preface the author urges all who have difficulty with this method of analysis to communicate directly with him; suggestions in regard to it will be welcomed and he will gladly analyze any substances with which the copper oxide method is unable to cope. J. B. T.

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[1] Hasenclever: Chem. Ind., 28, 52, quoted in Jahrbuch Chem., 1905, 373.

VORLESUNGEN ÜBER ANORGANISCHE CHEMIE FÜR STUDIERENDE DER MEDIZIN. Von DR. ERNST COHEN und DR. P. VAN ROMBURGH, Ordentliche Professoren an der Reichsuniversität zu Utrecht. Mit 68 Figuren nach Originalphotogrammen. Leipzig: Wilhelm Engelmann. 1906. pp. 431. Price, M. 15.

This is a text-book of inorganic chemistry of medium length, written in chapters called "lectures," although they are far too long to be actually used as such without subdivision. The reason offered by the authors for this arrangement is as follows:

"Those who know the great difficulties which the study of chemistry presents to the beginner, know that the desired result can only be reached by a 'frappez fort, frappez toujours.' As the material in this book is in the form of lectures, opportunity is given to bring the chief facts repeatedly before the student. To attain this result we have, in connection with a given substance, described the chief phenomena and the laws governing them at length, so that what has been thus learned may be easily applied to substances studied later, and we have not hesitated to repeat the explanation of the most important principles at suitable opportunity. For this reason more space is given to the fundamental laws of general chemistry than is usual in works designed for the same purpose as this."

On examining the book we find that the earliest substance treated of is water, and in the first 5 lectures, occupying 65 pages, the authors bring in (a propos of water) nearly all the theoretical chemistry they need, including, among other matters, atomic and molecular theories, vapor density determinations, reversible reactions, electrolytic dissociation, acids, bases and salts, acidimetry, alkalimetry and titration, endothermic and exothermic reactions, dissociation of gases, chemical equilibria, solution of gases and Henry's law. All this before the study of a single element! The sixth lecture takes up the study of oxygen and the remainder of the book, with a few exceptions, is purely descriptive. Practically, then, we find here the old German text-book arrangement; an opening section with theory, the rest descriptive. The book seems to be a hard one to study. The periodic system is dismissed in a few lines on the last 2 pages of the book as unsatisfactory, consequently the practical help in classification which it affords the student is lost. Why the book should be especially for students of medicine is not clear. There are no more references to properties of substances useful in medicine than in the average text-book.

On the other hand, it must be recognized that the book is very clearly and thoughtfully written, and that the medical student who succeeds in mastering it will have a respectable knowledge of chemical laws and of inorganic chemistry.

E. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Herausgegeben von RICHARD MEYER. XV Jahrgang, 1905. Braunschweig: F. Vieweg und Sohn. 1906.

This new volume of the *Jahrbuch* covers 595 pages. The list of co-workers is the same as last year, with the exception of Professor Werner, who has given up the review of inorganic chemistry. His place is filled by the well-known inorganic chemist, Professor K. A. Hofmann, of Munich.

The value of the *Jahrbuch* is so well established that it is only needful to say that the present volume maintains the standard of thoroughness of its predecessors. E. R.

DER NACHWEIS VON SCHRIFTFÄLSCHUNGEN, BLUT, Sperma, u. s. w. unter Besonderer Berucksichtigung der Photographie. Von PROF. DR. M. DENNSTEDT und DR. F. VOIGTLÄNDER. Braunschweig: Friedrich Viewig und Sohn. 1906.

A work by the same authors, bearing upon the same general subject, was recently reviewed.[1] The present volume deals with the detection of adulterations in handwriting, with special reference to the use of photography. The technique of the processes is described in full, and numerous micro-photographical representations of fraudulent handwriting are used to exemplify the methods given. The question of the obliteration of the original handwriting is treated in detail and especially the bleaching materials which are employed. Imitations of handwriting are dealt with at great length and in detail, both by chemical and photo-microscopical processes. An interesting chapter is devoted to the micro-chemical examination of blood spots and of thumb prints. Analysts and experts will find this book extremely helpful, especially in the preparation of photographs for forensic purposes.

H. W. WILEY.

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[1] THIS JOURNAL, 36, 221 (1906).

AN ELEMENTARY STUDY OF CHEMISTRY. By WILLIAM MCPHERSON, PH.D., Professor of Chemistry, Ohio State University, and WILLIAM EDWARDS HENDERSON, PH.D., Associate Professor of Chemistry, Ohio State University. Revised Edition. Boston and New York: Ginn & Co. 1906.

This manual has been in use—in privately printed form—for 3 years at the Ohio State University. After such revision as experience suggested, it is now offered to the public. It is a book of the size and scope of Remsen's "Briefer Course," and contains at the close a chapter on simple organic compounds.

At first sight the book would seem not to differ essentially from several other manuals, but a close examination shows that it is written with marked ability and great care. The chapter on molecular and atomic weights and other chapters on theory are remarkably good and clear. The dissociation theory is applied throughout the book wherever it serves to explain phenomena; the older definitions of acids, bases and salts are replaced by definitions in terms of the theory.

While the descriptions of technical methods are necessarily very brief, they are modern and accurate.

The book can be cordially recommended as an excellent manual for high schools and for elementary college work.

E. R.